Monitored Natural Attenuation and Enhanced Retention Processes to Manage PFAS in Groundwater

NEWMOA: The Science of PFAS Conference



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AGENDA

- **PFAS = Bizzarro World?**
- Potential Futures for PFAS MNA
- Retention-Based MNA for PFAS
- Key Retention Processes
- Wait There's More! Enhanced Attenuation (EA)

What is the Philosophy Behind MNA?

It is harder and more expensive to clean these sites up than first thought.

Nature is amazing and seems to be degrading or sequestering some of these chemicals.

Let's let nature do the job.

But you have to do three things:



Nature

can help!



Understand







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PFAS = 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







PFAS = Bizarro World for Groundwater People?

- Little or no in-situ degradation of regulated PFAAs!
- > Biodegradation doesn't help, it hurts!
- Front-line technology is Pump and Treat? Are we back in the 1980s?
- Concentrations: single digit Nanogram per liters?
- > Thousands of individual PFAS!
- > 40,000+ sites? (EBJ, 2019)



Key Point: "Business as Usual" won't work for PFAS Groundwater Cleanup



Potential Futures for PFAS Management?

- **Scenario 1:** Pump & Treat is the predominant approach for PFAS plumes (with some injected sorbents)?
- Scenario 2: Researchers deliver a "silver bullet" that destroys PFAS in-situ, it is rapidly adopted.
- **Scenario 3:** Risk / Triage strategy used with variety approaches, including retention-based MNA at some sites.





Nothing Yet

PFAS Experts:

Most likely



Distill it Down to this Problem Statement

- > PFAS remediation is daunting challenge.
- Stringent criteria and lack of degradation has led to a general presumption that MNA doesn't work for PFAS.
- If true, thousands of expensive pump and treat systems may be needed.
- However, we feel there is a viable path for some sites towards PFAS MNA based on PFAS retention.
- One analog: MNA of metals/inorganics/radionuclides based on immobilization onto aquifer solids (no degradation).



EPA's Guidance MNA for Metals and Rads Lead to DOE's "Scenarios" Guidance



<u>Six geochemical scenarios</u> (based on ORP, CEC, SIO) for <u>19 Inorganic /</u> <u>radionuclide contaminants</u> determine Mobility for MNA purposes

	Scenarios					
Contaminant	Scenario 1 low ORP high CEC	Scenario 2 Iow ORP Iow CEC	Scenario 3 high ORP high CEC high SIO ¹	Scenario 4 high ORP high CEC Iow SIO ¹	Scenario 5 high ORP low CEC high SIO ¹	Scenario 6 high ORP low CEC low SIO ¹
Cr(III)	lis	lis				
Cr(VI)	reduced to Cr(III)	reduced to Cr(III)				
⁹⁹ Tc(IV)	JS	↓S	Likely oxidized to Tc(VII)	Likely oxidized to Tc(VII)	Likely oxidized to Tc(VII)	Likely oxidized to Tc(VII)
⁹⁹ Tc(VII)	reduced to Tc(IV)	reduced to Tc(IV)				
Pu						
U						
Cd, Cu, Pb, Zn	S	l⊃ls				
Ni	S	l□□↓s				
As	JS	↓s				
Se						
⁹⁰ Sr, Cs ² , Ra ³	↑TDS			H H	IIGH Mobi	lity
NO ₃ ⁻ , CIO ₄ ⁻ ¹²⁹ I	can degrade	can degrade			NEDIUM M OW Mobil	lobility ity

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Monitored Natural Attenuation for PFAS?

Key Inspiration: High-resolution sampling, matrix diffusion modeling for ESTCP project ER-201633, NAVFAC PFAS Project.

Key Result: Over 75% of PFAS mass in saturated zone is retained in low-permeability units.

Key Points:

- Significant PFAS mass is retained in saturated zone
- Other PFAS researchers show significant retention on ٠ air/water, NAPL/water interfaces
- PFAS will sorb •
- We can integrate these together to understand MNA



Monitored Natura Impacts to Groun	Il Attenuation to Manage PFA dwater: Scientific Basis
by Charles J. Newell ©, David T. Adar Jovan Popovic and Hans F. Stroo	son, Poonam R. Kulkarni, Blossom N. Nzeribe, John A. Connor,
DOI: 10.1002/rem.21697	
RESEARCH ARTICLE	WI
Monitored natural atte to groundwater: Poter	enuation to manage PFAS impacts ntial guidelines
	Adamson ¹ Poonam R. Kulkarni ¹



Key PFAS MNA Processes



PFAS Source



Newell et al, 2021

Key Vadose Zone Retention Processes – Air/Water Partitioning

- PFAS are surfactants
- They like to accumulate at air/water interfaces
- This can retain some PFAS in the unsaturated zone for a long time
- Depends on site, but "can take several decades or longer for PFOS to reach groundwater."

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Key Saturated Zone Retention Processes – Sorption and Matrix Diffusion



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





PFAAs don't readily degrade, so there may be more **expanding PFAS plumes.**

But matrix diffusion is retaining PFAS, therefore slowing plume expansion

Key PFAS Retention Processes – **Chemical Retention**



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- Most regulated PFAS are Perfluoroalkyl Acids (PFAAs)
- Examples: PFOS, PFOA, PFHxS
- The biodegradation of precursors can form PFAAs, the terminal compound in the degradation pathway
- PFAAs are often more mobile than precursors
- "Chemical retention" is a general term for when PFAAs are left in the more environmental benign precursor state

How Might Retention-Based PFAS MNA affect Plumes?

- Apply matrix diffusion model to extremely well characterized PFAS sites
- *Key Point: attenuation affect of matrix diffusion on plume migration seen at this site*



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How Might Retention-Based PFAS MNA Affect Plumes?

GSI Contents lists available at ScienceDirect ENVIRONMENTAL Journal of Contaminant Hydrology journal homepage: www.elsevier.com/locate/jconhyd Impact of matrix diffusion on the migration of groundwater plumes for Perfluoroalkyl acids (PFAAs) and other non-degradable compounds Shahla K. Farhat^{a,*}, Charles J. Newell^a, Sophia A. Lee^b, Brian B. Looney^c, Ronald W. Falta^d Transmissive Homogeneous Transmissive Aquifer With Aquitards With 80% Lenses Transmis Transmissive Transmissive *MAKAZAA*meters*a*ma

1040 meters

250 meters

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Modeling Studies to Explore Retention-Based PFAS MNA

> PFOS Plume Length after 100 years:

1310 meters

Wait – There's More!





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Enhanced Attenuation (EA)



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



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Injection of Particulate Sorbents. Status: Being Done Now



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Capping to Increase Retention in the Vadose Zone. Status: Being Done Now



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Emplacement of LNAPL Sorption Barrier. Status: Proposed for Research Project



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Injection of Emulsified Oil to Enhance Chemical Retention. Status: Proposed for Research Project

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WRAP UP

- **PFAS in groundwater is a daunting challenge**
- No proven in-situ PFAS destructive technologies means "not business as usual"
- Retention-Based PFAS MNA may be useful for some sites
 - Sites with long travel time to receptors/compliance point
 - Sites with relatively lower mass flux
- Data requirements for evaluat MNA and gather lines of evidence are likely to be significant
- At other sites, Enhanced Attenuation (EA) approaches may be useful
- But time will tell!



QUESTIONS



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