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In-situ PFAS immobilization for groundwater plume control:
Challenges for the applicability
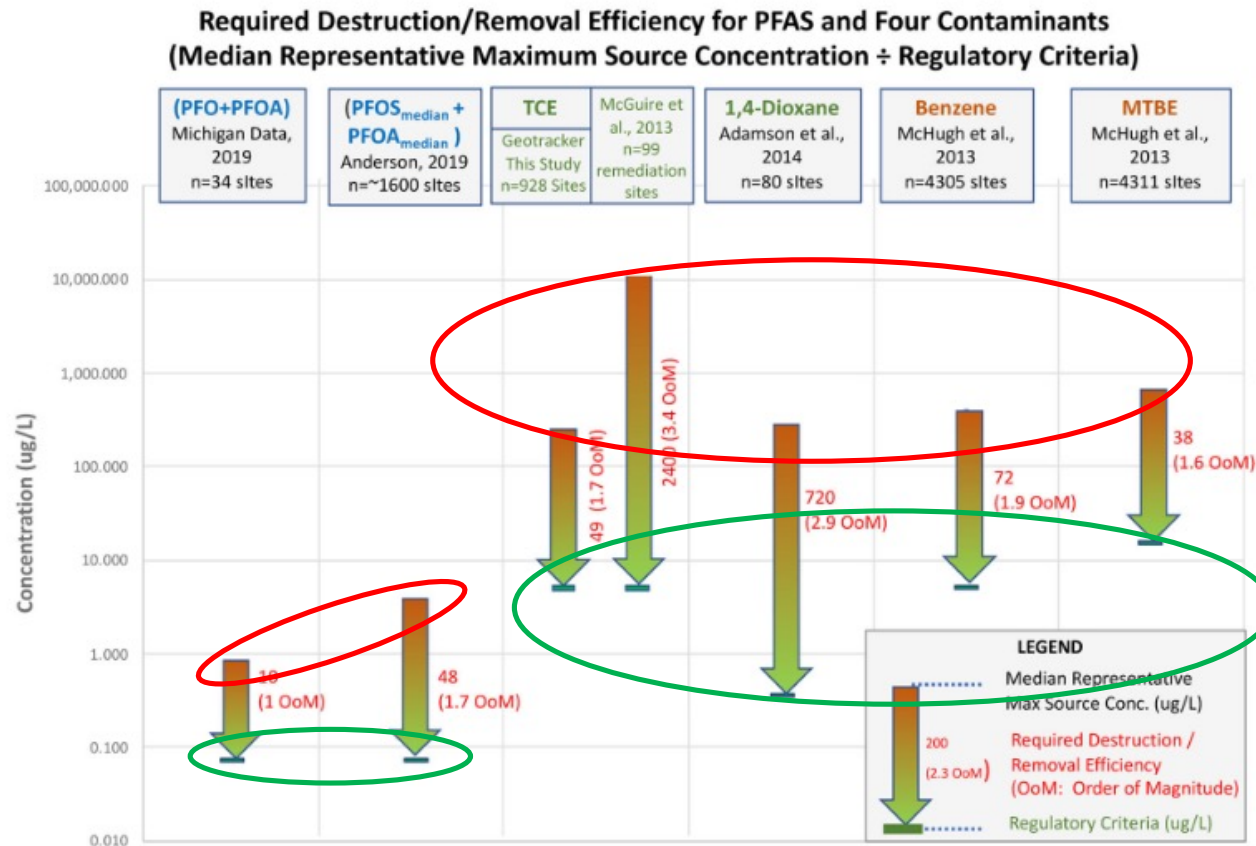
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In situ PFAS immobilization: Why ?

Required Destruction/Removal Efficiency for PFAS and Four Contaminants
(Median Representative Maximum Source Concentration ÷ Regulatory Criteria)

Source: Newell et al. (2020), *Comparing PFAS to other groundwater contaminants: Implications for remediation*

1. Low concentrations:
➔ Low « source » concentrations
➔ Low remedial « target » concentrations

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In situ PFAS immobilization: Why ?

TABLE 10 Summary of nine quantitative metrics related to potential scale of groundwater remediation from Tables 2 to 7. A: Absolute data for metrics (From Tables 2–7). B: Relative data for metrics

	CVOCs	1,4-Dioxane	Benzene	MTBE	PFAS
A. Absolute data for metrics					
Total Production (tonnes)	2.2×10^7	1.7×10^5	1.9×10^8	1.4×10^8	2.6×10^4
Estimated number of groundwater sites	53,000	23,000	560,000		42,560
Frequency detect public water supply	18%[a]	12%	1.3%	15%	1.0%
Attenuation indicator: Plume length (ft)	1000	880	130	75–140	1,250[b]
Hydrophobic sorption R (−)	2	1.1	1.3	1.1	1.5–6[c]
Regulatory criteria (µg/L)	5	0.46	5	13	0.070
Required destruction/removal efficiency	49–2400	720	72	38	10[d]
Relative remediation capability	10	–	3.1	–	0
Relative research intensity	432	–	–	–	927
B. Relative data for metrics					
Total production (tonnes)	850	6.2	730	5400	1
Estimated number of groundwater sites	1.3	0.5	13		1
Frequency detect public water supply	18	12	1.3	15	1
Attenuation indicator: Plume length (ft)	0.80	0.70	0.10	0.11	1
Hydrophobic sorption R (−)	1.3	0.73	0.87	0.73	1[e]
Regulatory criteria (µg/L)	71	6.5	71	186	1
Required destruction/removal efficiency	4.9–240	72	7.2	3.8	1
Relative remediation capability	10	–	3.1	–	0[f]
Relative research intensity	0.46	–	–	–	1

Abbreviations: CVOC, chlorinated volatile organic compound; MTBE, Methyl tert-butyl ether; PCE, perchloroethene; PFOA, perfluorooctanoic acid; PFAS, per- and polyfluoroalkyl substances; PFOS, perfluorosulfonic acid; TCE, trichloroethene.
[a]PCE value was used to represent CVOCs.
[b]Chloride plumes used as a nondegrading proxy.
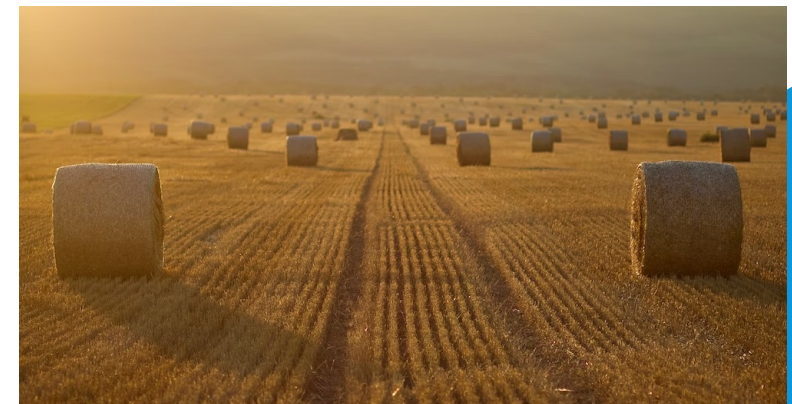[c]For PFOA and PFOS, respectively.
[d]Michigan PFAS dataset.
[e]Based on PFOA R = 1.5.
[f]Reporting absolute value because PFAS assumed to be zero.

Source: Newell et al. (2020), *Comparing PFAS to other groundwater contaminants: Implications for remediation*

2. Large plume dimensions

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In situ PFAS immobilization: Why

Table 1. Comparison of published PFAS destruction technologies investigation on water media.

| Technology	AFFF	Still Bottom	Synthetic	PFASType	C_i (µg/L)	C_f (µg/L)	T (h)	Vol (L)	DE (%)	Energy Consumed (kWh/m³)	Mass of PFAS Destroyed (kg)	Energy per Mass (kWh/kg)	Ref.
Electrochemical Oxidation				Multi	1652	4.2	10	2	99.7412	256	3.2×10^{-6}	1.6×10^5	[35]
				PFHxA	870,000	87,000	1.5	1	90.0000	15.2	7.8×10^{-4}	1.9×10^1	[52]
			x	Multi	451	50.6	8	0.3	88.7804	99	1.0×10^{-7}	2.5×10^5	[45]
	x			Multi	539	126.4	8	0.3	76.5491	136	1.0×10^{-7}	3.3×10^5	[45]
		x		PFOA	3050	897	80	0.56	70.5902	0.161	1.21×10^{-6}	3.98×10^7	[44]
		x		PFOA	4080	609	80	0.415	85.0735	0.131	1.44×10^{-6}	3.33×10^7	[44]
		x		PFOS	4420	538	80	0.56	87.8281	0.094	2.17×10^{-6}	2.21×10^7	[44]
		x		PFOS	15,200	361	80	0.415	97.6250	0.071	6.16×10^{-6}	7.79×10^6	[44]
		x		8:2 FTS	193	50	120	0.56	74.0933	0.146	8.01×10^{-8}	5.99×10^8	[44]
		x		8:2 FTS	753	125	120	0.415	83.3997	0.148	2.61×10^{-7}	1.84×10^8	[44]
Sonochemical Degradation			x	PFOS	5001	0	3	0.6		208	3.0×10^{-6}	4.2×10^4	[103]
			x	PFOA	4141	0	2	0.6		208	2.5×10^{-6}	5.0×10^4	[103]
			x	PFOS	10,000	7200.0	1	0.1	28.0000	3333	1.7×10^{-7}	1.2×10^6	[100]
			x	PFOA	10,000	3700.0	1	0.1	63.0000	3333	3.8×10^{-7}	5.3×10^5	[100]
			x	PFOS	100	5	2.3	0.6	95.0000	448	5.7×10^{-8}	4.7×10^6	[148]
			x	PFOA	100	28	2.3	0.6	72.0000	1050	4.3×10^{-8}	1.5×10^7	[148]
			x	PFOS	9420	96	4		99.9898				[102]
			x	PFOS	9420	133	4		99.9858				[102]
			x	PFOS	9420	177	4		99.9812				[102]
			x	PFOA	140	1.2	4	2	99.1428				[113]

Source: Meegoda et al. (2022), *A review of PFAS Destruction Technologies*

3. Applicable *in situ* destruction /degradation techniques not available (yet)

- Low efficiency (low concentrations)
- Extremely high energy consumption (environmental impact?!)
- Prior concenter phase needed (increasing the « hit ratio »)

After: CDM Smith

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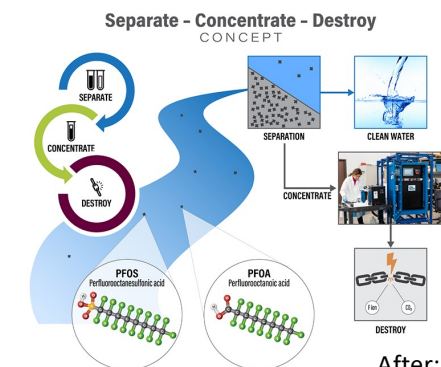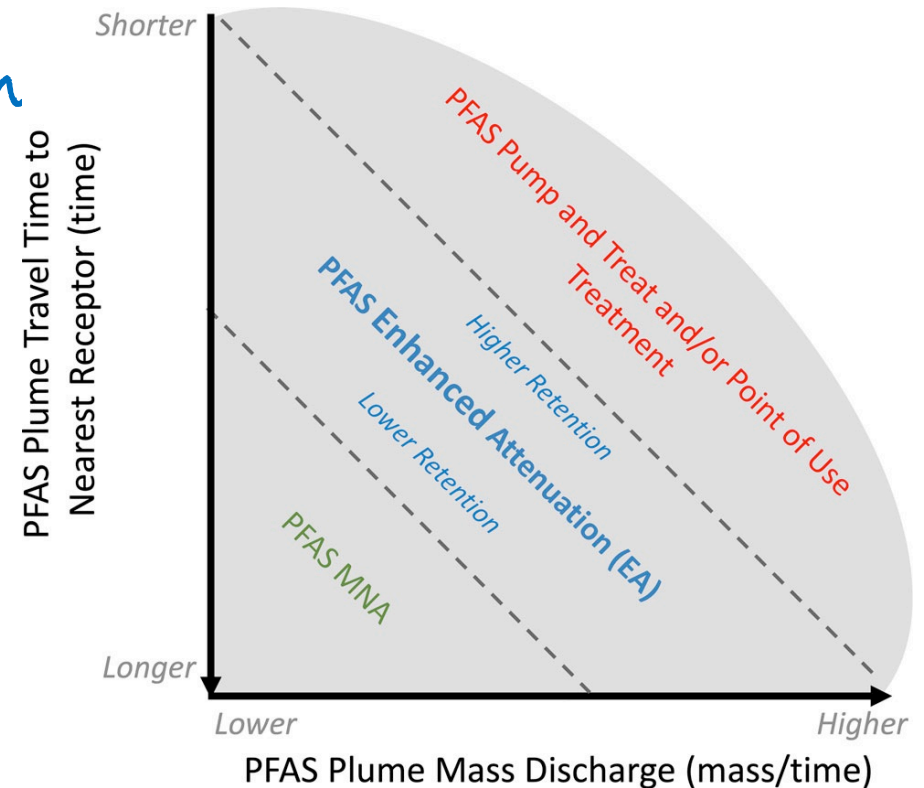
In situ PFAS immobilization

1. Low concentrations:
➔ Low « source » concentrations
➔ Low remedial « target » concentrations

2. Large plume dimensions

3. *In situ* destruction /degradation techniques not available (yet)
➔ Low efficiency (low concentrations)
➔ Extremely high energy consumption (environmental impact?!)
➔ Prior concenter phase needed (increasing the « hit ratio »)

PFAS Plume Travel Time to Nearest Receptor (time)

Shorter

Longer

PFAS Pump and Treat and/or Point of Use Treatment

Higher Retention

PFAS Enhanced Attenuation (EA)

Lower Retention

PFAS MNA

Lower

Higher

PFAS Plume Mass Discharge (mass/time)

Need for an extensive, passive, low energy consuming, long-term, irreversible PFAS « treatment » technique to reduce the dispersion risk (« Enhanced attenuation »)

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Source: Newell et al. (2022), *Enhanced attenuation (EA) to manage PFAS plumes in groundwater*

In situ PFAS immobilization: What ?

Increasing the **retardation** of PFAS by inducing a shift from **soluble** state **to sorbed** state by the **addition of an immobile sorbent**

Retardation coefficient:

$$R = 1 + \frac{\rho_d}{\sigma} K_f \frac{1}{n} C^{\frac{1}{n-1}}$$

Freundlich sorption isotherm :
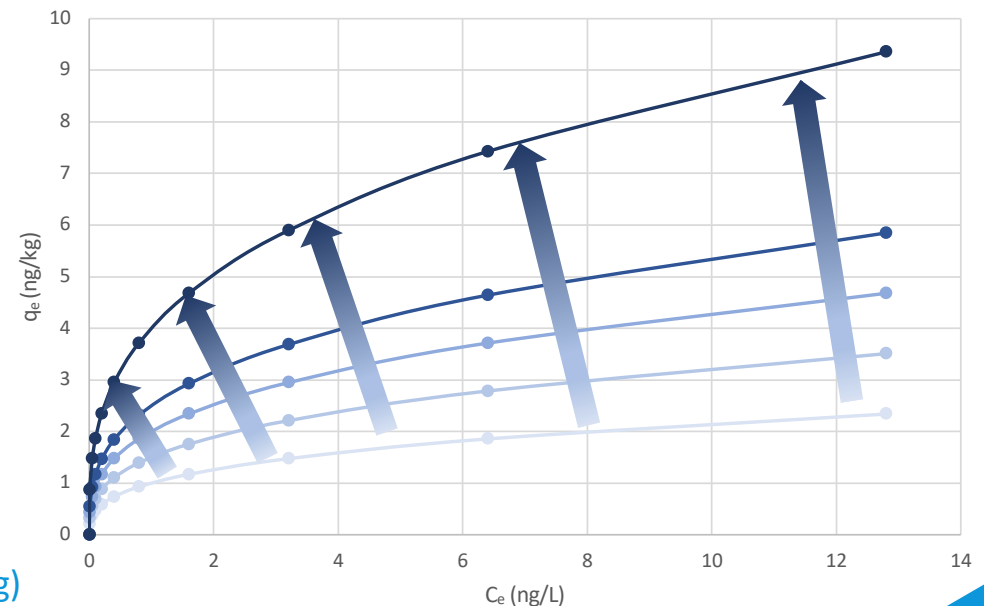
$$q_e = K_f \bullet C_e^{(1/n)}$$

→   With: q_e = sorbed concentration (mg/kg)
             K_f = Freundlich sorption coefficient (mg/kg [mg/L]-a)
             C_e = equilibirum aqueous concentration (mg/L)
             (1/n) = exponent depending on linearity of isotherm

In situ PFAS immobilization: What ?

Multiple sorption mechanisms:

A: Electrostatic attraction
B: Electrostatic repulsion
C: Electrostatic repulsion
D: Divalent-bridge effect
E: Hydrophobic interaction
F: Hemi-micelle structure
G: Micelle structure
H: Anion exchange

PFAS

NOM Natural organic matter

Different sorbents reported:

Activated carbon (GAC, PAC, CAC)
Biochar
Hydrophobic (cationic) polymers

Ion exchange resins (IX)
Layered double hydroxides (LDH)

Organoclays
Zeolites
Aluminum oxyhydroxides

Source: Lei et al. (2023), *A revieuw of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities*

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In situ PFAS immobilization: Current ch

Closing the gap between **lab test** results and **field** application

- Full contact: perfectly homogenized
- Prolonged contact time
- Closed reactor
  - No influx of fresh (ground)water
  - Fixed ratio sorbent/groundwater might influence geochemistry of (ground)water
  - Leaching of sorbent impossible
- Limited number of (known) PFAS compounds and concentrations
- No or limited number of co-contaminants

Source: Lei et al. (2023), *A revieuw of PFAS adsorption from aqueous solutions: Current approaches, engineering applications, challenges, and opportunities*

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In situ PFAS immobilization: Current challenges ?

Closing the gap between **lab test** results and **field** application

Source: Lei et al. (2018) *Mechanism and implication of sorption of perfluorooctanoic acid by varying soil size fractions*

- Challenges to achieve full contact
- limited contact time (tried to be increased with barrier width)
- "continuous flow-through" reactor
    - influx of fresh (ground)water
    - ratio sorbent/groundwater gradually decreases (longevity effect)
    - Possible leaching of sorbent
- Unknown (and changing) PFAS composition and concentration (over time and place) (cfr. "*chromatographic*" *fractionation*)
    - Competition between compounds
    - Reversible sorption (exchange of one compound for another)
    - Desorption in case of lowering influx concentration
- multiple co-contaminants and natural substances
    - Competition for available sorption sites (e.g. humic acids, CVOCs)
    - DOM-associated PFAS + colloid-associated PFAS with completely different sorption behaviour than "pure" PFAS-form
    - PFAS sorption influenced by pH, salinity and salt composition

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In situ PFAS immobilization: Current cha

How to achieve **full contact** between sorbent and (migrating) PFAS ?

Sorbents need to **migrate easily** in **natural porosity** of the soil during injection,
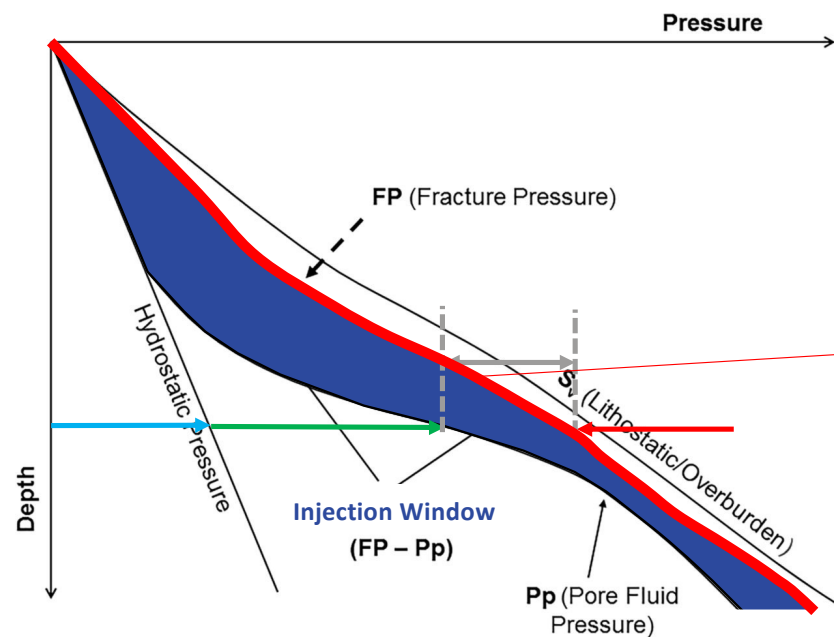but **stay immobile** after injection to prevent leaching of sorbent

In situ PFAS immobilization: Current cha

How to achieve **full contact** between sorbent and (migrating) PFAS ?

Sorbents need to **migrate easily** in **natural porosity** of the soil during injection,
but **stay immobile** after injection to prevent leaching of sorbent

Injection pressure window depends on :
    Soil depth
    Groundwater level
    Pore dimensions (soil texture)
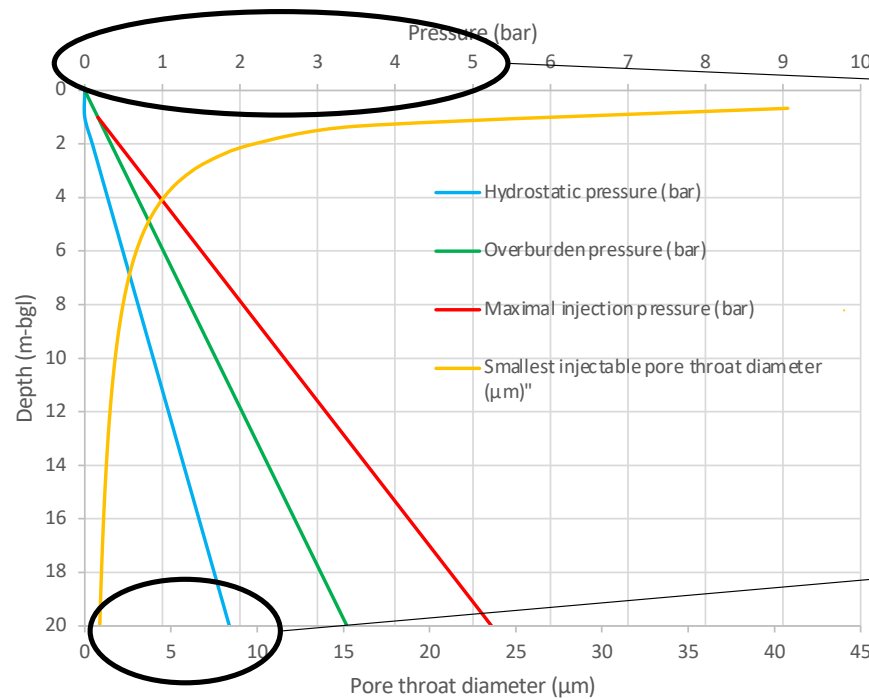
Maximum injection pressure determines
the **lower limit of the "injectable"**
pores (pore throat diameter)

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In situ PFAS immobilization: Current cha

How to achieve **full contact** between sorbent and (migrating) PFAS ?

Sorbents need to **migrate easily** in **natural porosity** of the soil during injection,
but **stay immobile** after injection to prevent leaching of sorbent

Low injection pressure

But high flow rate to prevent precipitation !

Maximum injection pressure determines
the **lower limit of the "injectable"**
pores (pore throat diameter)

Only pores > 1 – 10 μm

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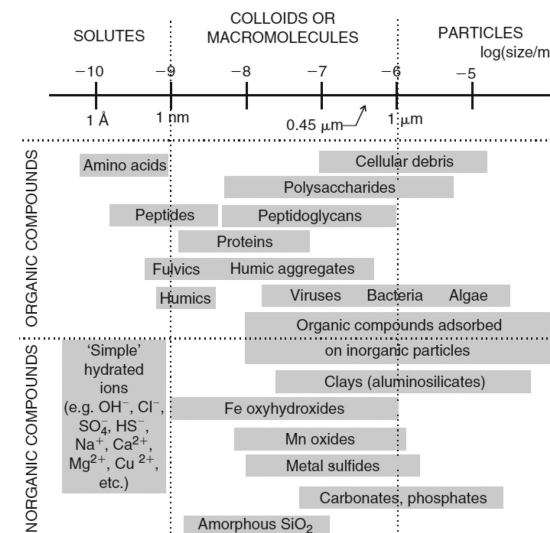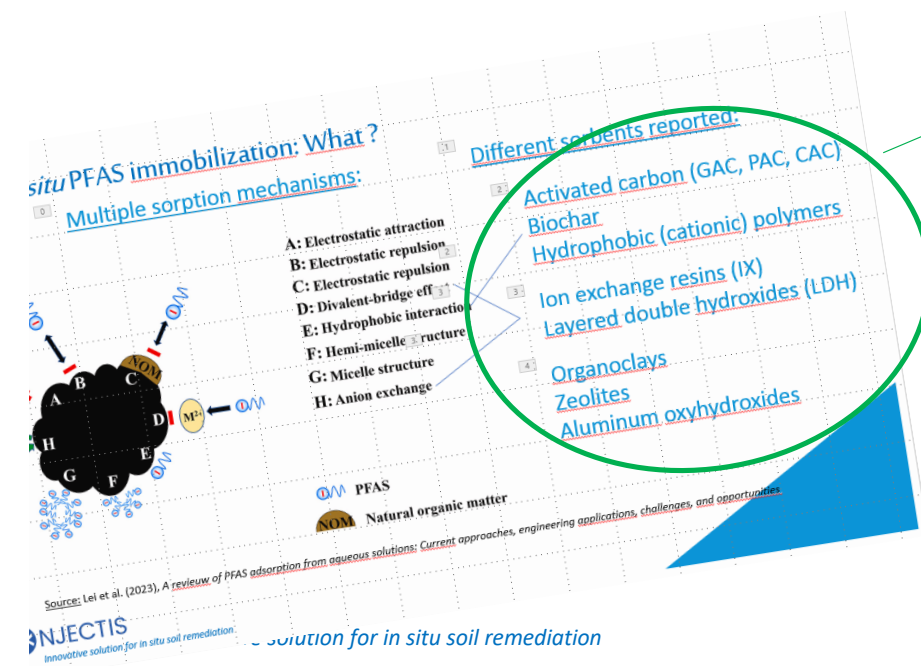# In situ PFAS immobilization: Current cha...

How to achieve **full contact** between sorbent and (migrating) PFAS ?

Sorbents need to **migrate easily** in **natural porosity** during injection,
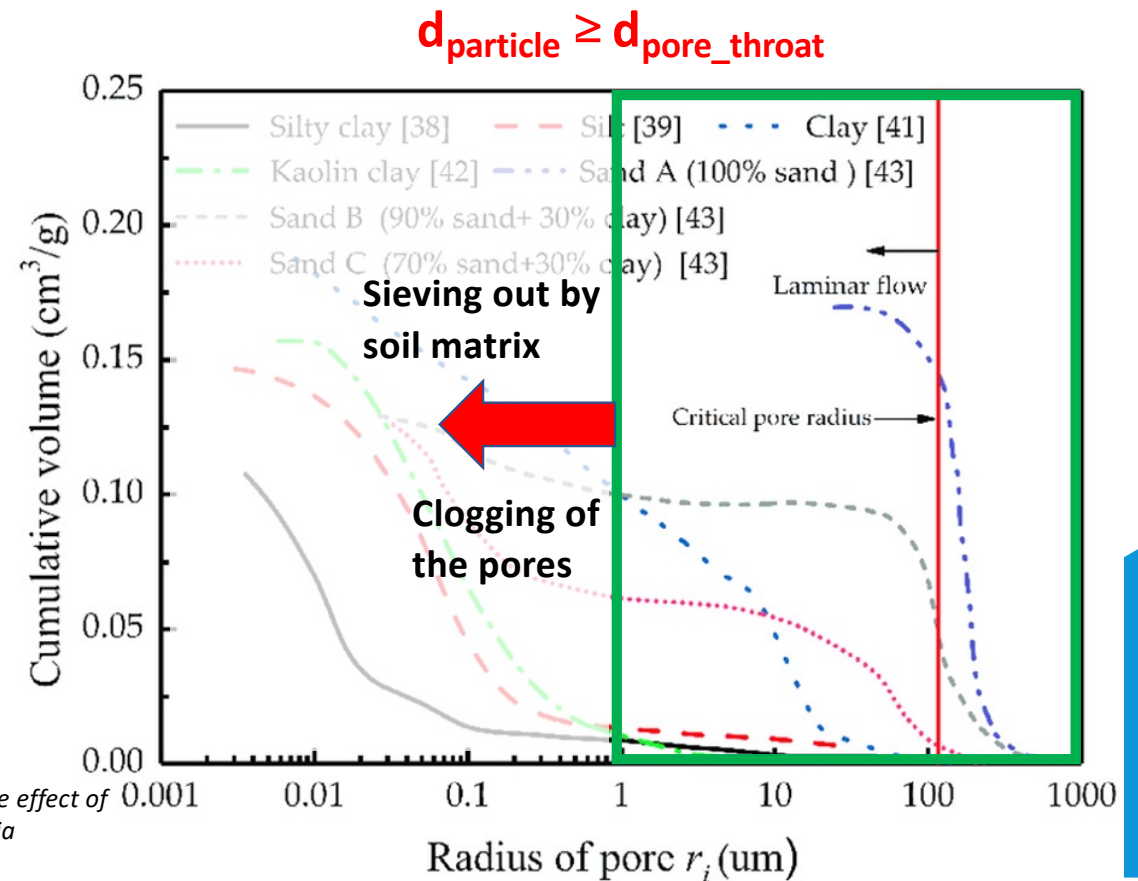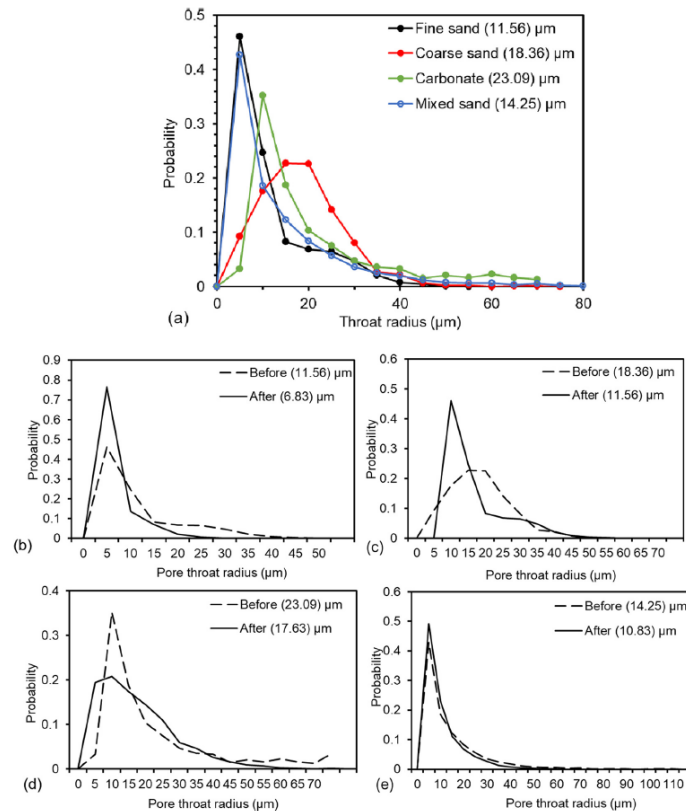but stay **immobile** after injection to prevent leaching of sorbent

Majority of sorbents = particulate
colloids or particle suspension (1 nm – 100 µm)

In situ PFAS immobilization: Current challenges ?

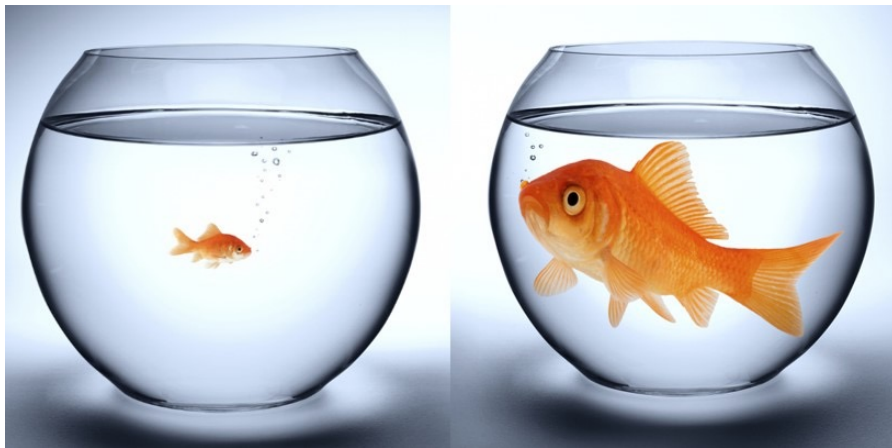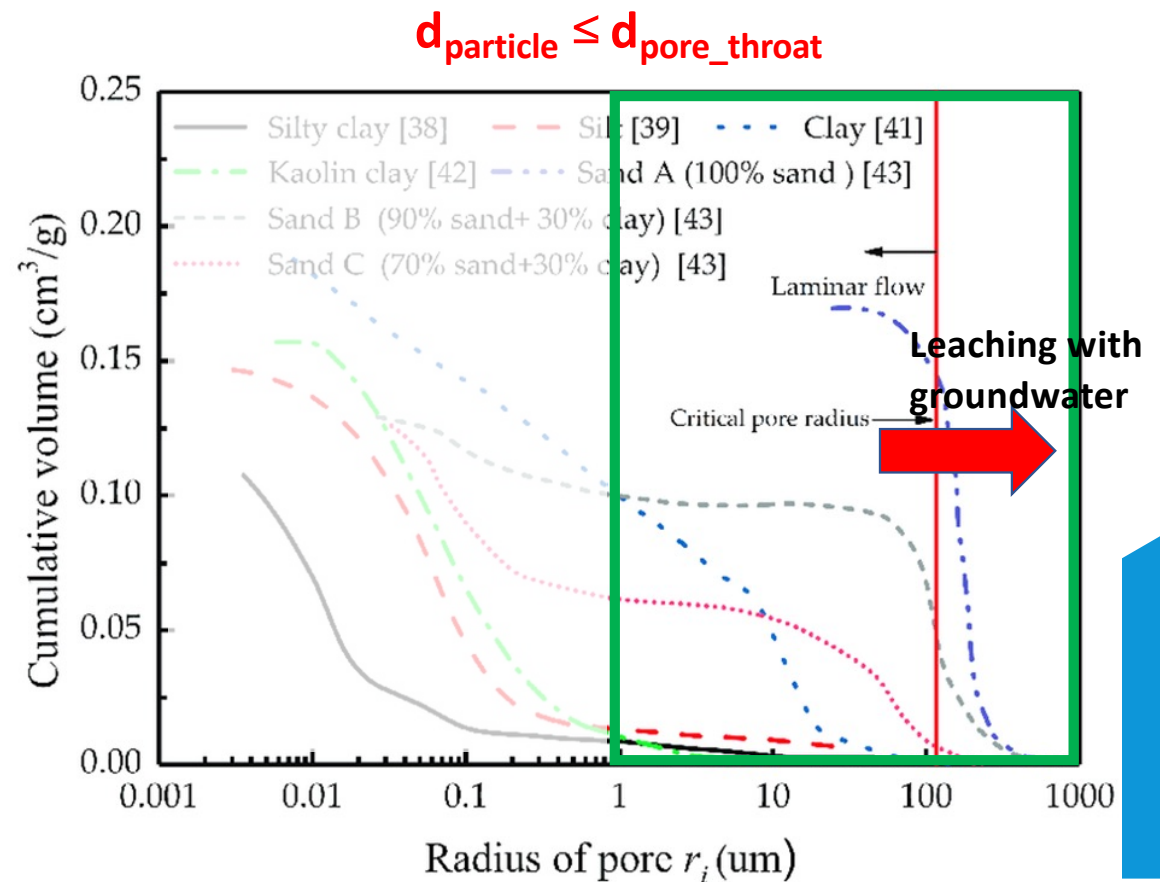How to achieve **full contact** between sorbent and (migrating) PFAS ?

$d_{particle} \geq d_{pore\_throat}$

Sieving out by soil matrix

Clogging of the pores

Source: Fopa et al. (2023) *A pore-scale investigation of the effect of nanaparticle injection on properties of sandy porous media*

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In situ PFAS immobilization: Current challenges ?

How to achieve **full contact** between sorbent and (migrating) PFAS ?

One size does not fit all!

$d_{particle} \leq d_{pore\_throat}$

Leaching with groundwater

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In situ PFAS immobilization: Current ch

How to achieve **full contact** between sorbent and (migrating) PFAS ?

Sorbents need to **migrate easily** in **natural porosity** during injection,
but stay **immobile** after injection to prevent leaching of sorbent

Different "sorbent immobilization" mechanisms:
- Physical sieving out in smaller pores (clogging?)
- Settling as a result of lowering water velocity ($v_{injection} \gg v_{groundwater}$)
- Interaction with soil matrix (e.g. cation bridging with clay, hydrophobic sorption to NOM)
- In situ particles formation /precipitation ???
- Swelling of particles after injection ???

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Thank you

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