THE EMERGING ISSUE

PFAS POLY- AND PERFLUOROALKYL SUBSTANCES

Big Picture, Challenges and Solutions

August 2016

Ian Ross Ph.D.
ARCADIS

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Health & Safety Moment

Hydrogen Peroxide is Rocket Fuel

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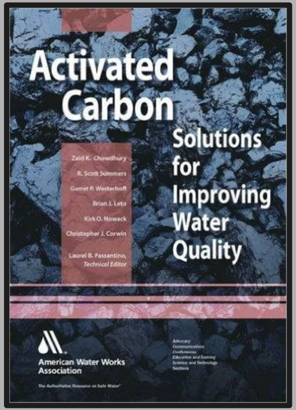
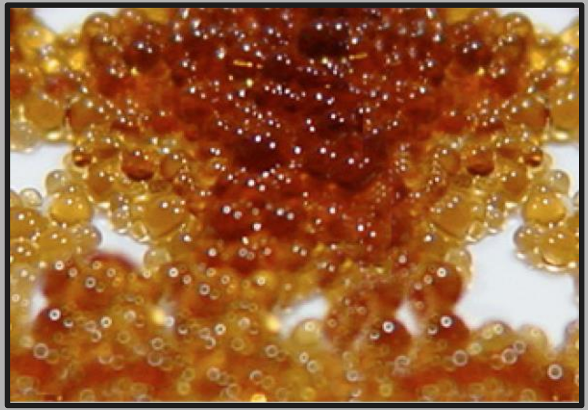
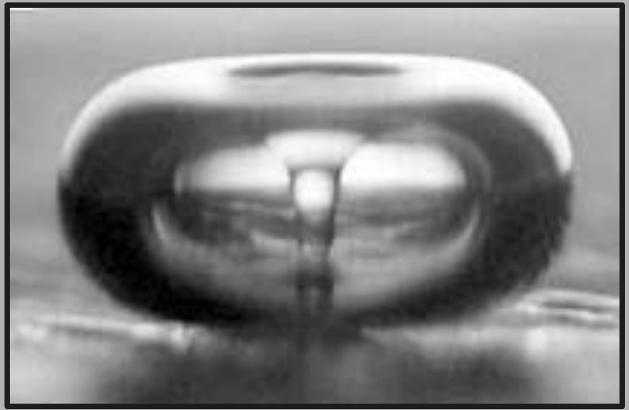
Treatment and Restoration







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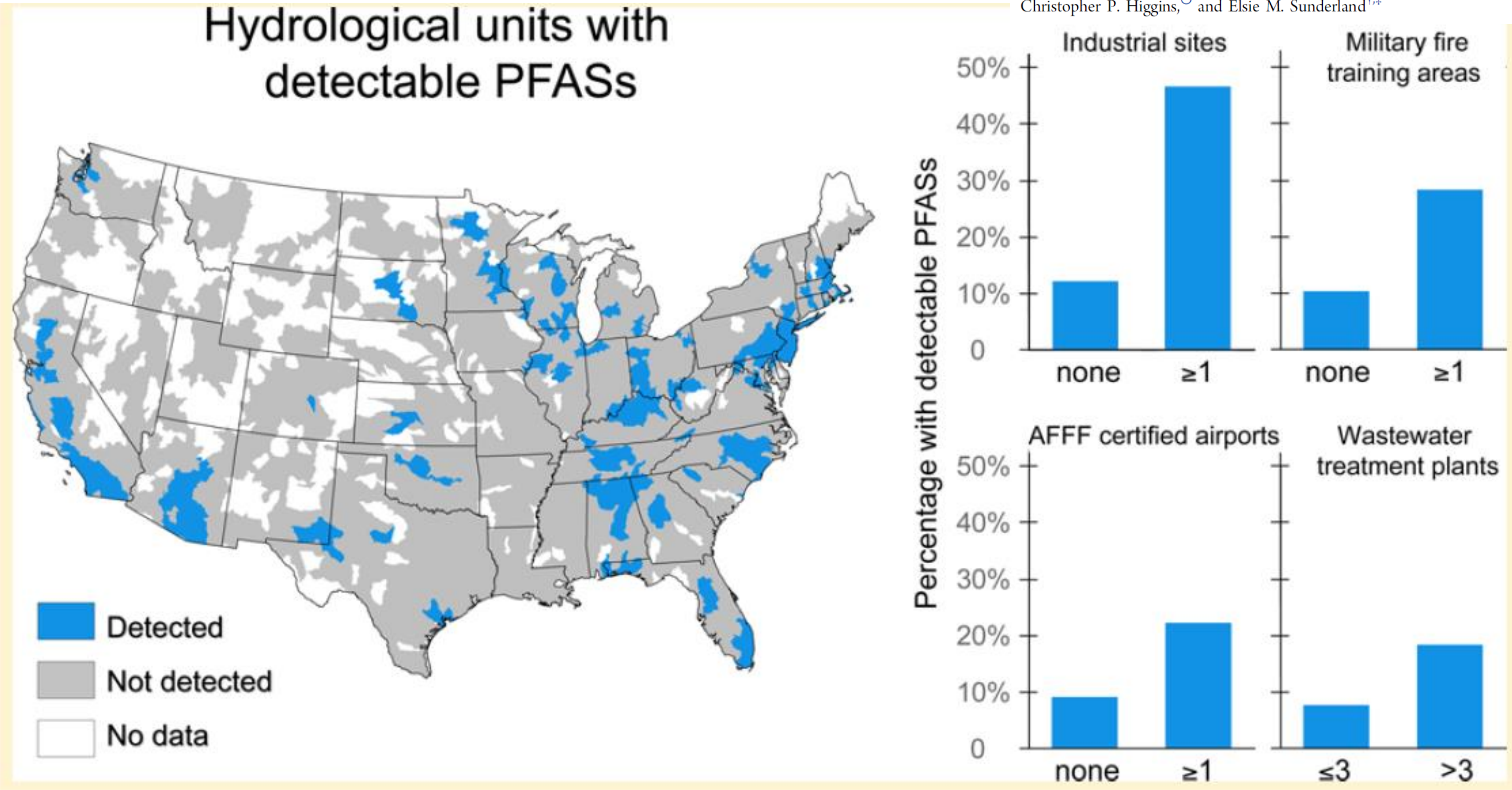
Impacted Water

Environmental Science & Technology Letters
Letter
pubs.acs.org/journal/estlcu

Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

Xindi C. Hu,[*,†,‡] David Q. Andrews,[§] Andrew B. Lindstrom,[∥] Thomas A. Bruton,[⊥] Laurel A. Schaider,[#] Philippe Grandjean,[†] Rainer Lohmann,[@] Courtney C. Carignan,[†] Arlene Blum,[⊥,∇] Simona A. Balan,[●] Christopher P. Higgins,[○] and Elsie M. Sunderland[†,‡]

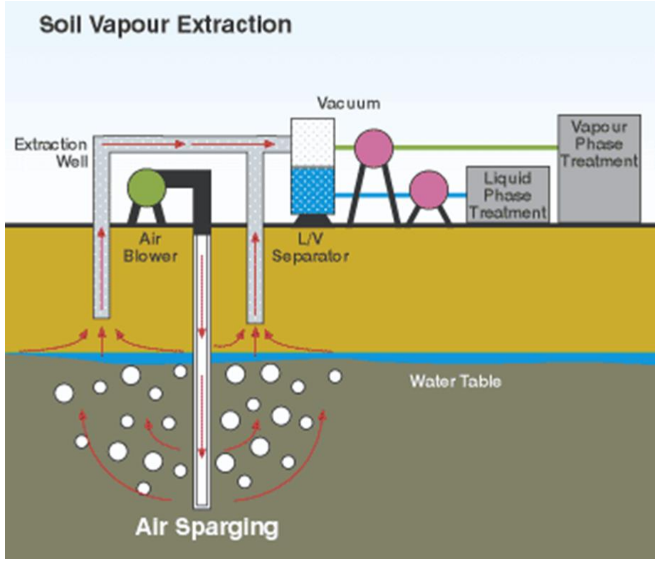


REMEDIATION / WASTE TREATMENT

Ex-Situ: ‘Out of Ground’ Solution

In-Situ: ‘In Ground’ Solution

Combination: Phased Approach



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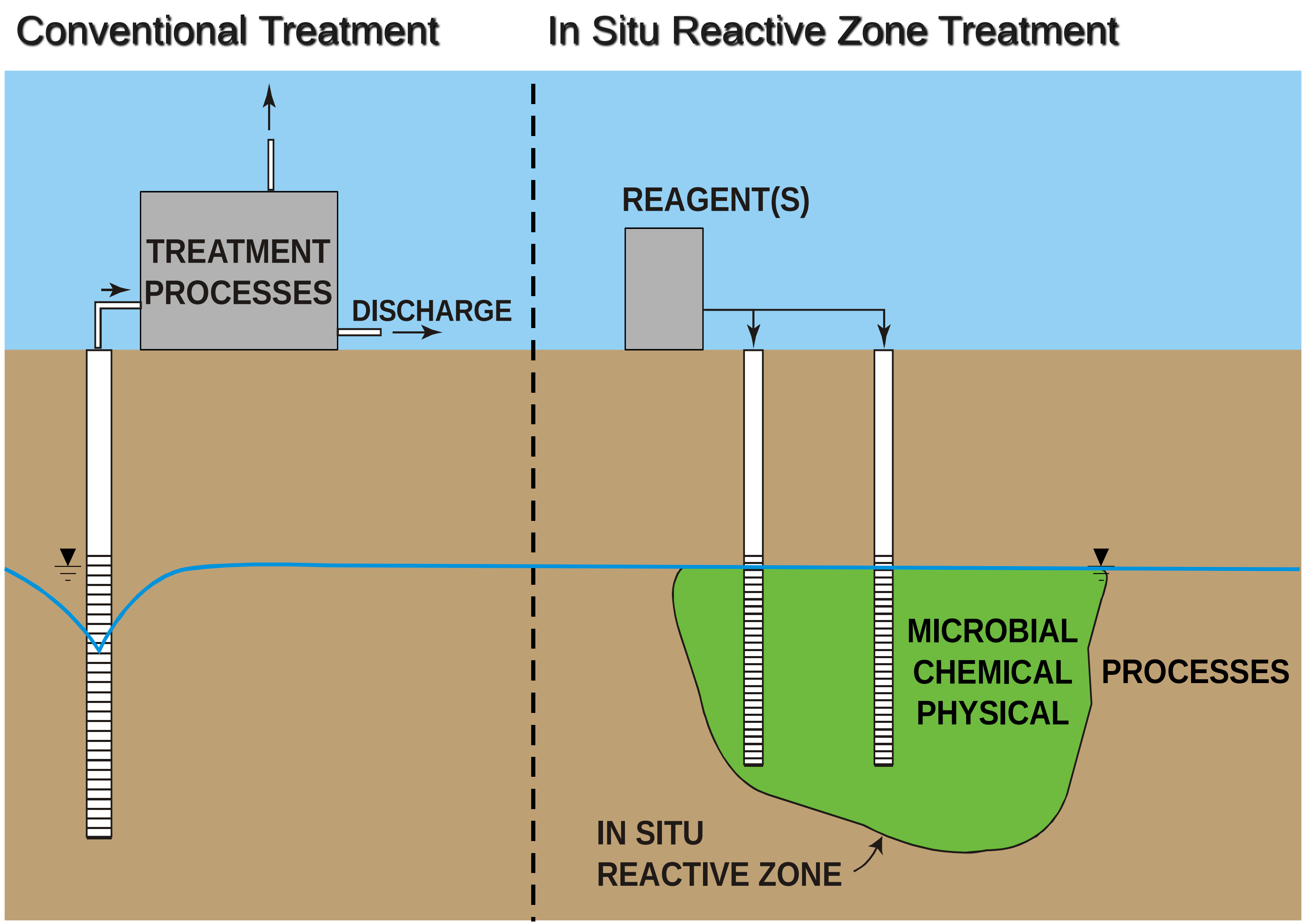
Remediation



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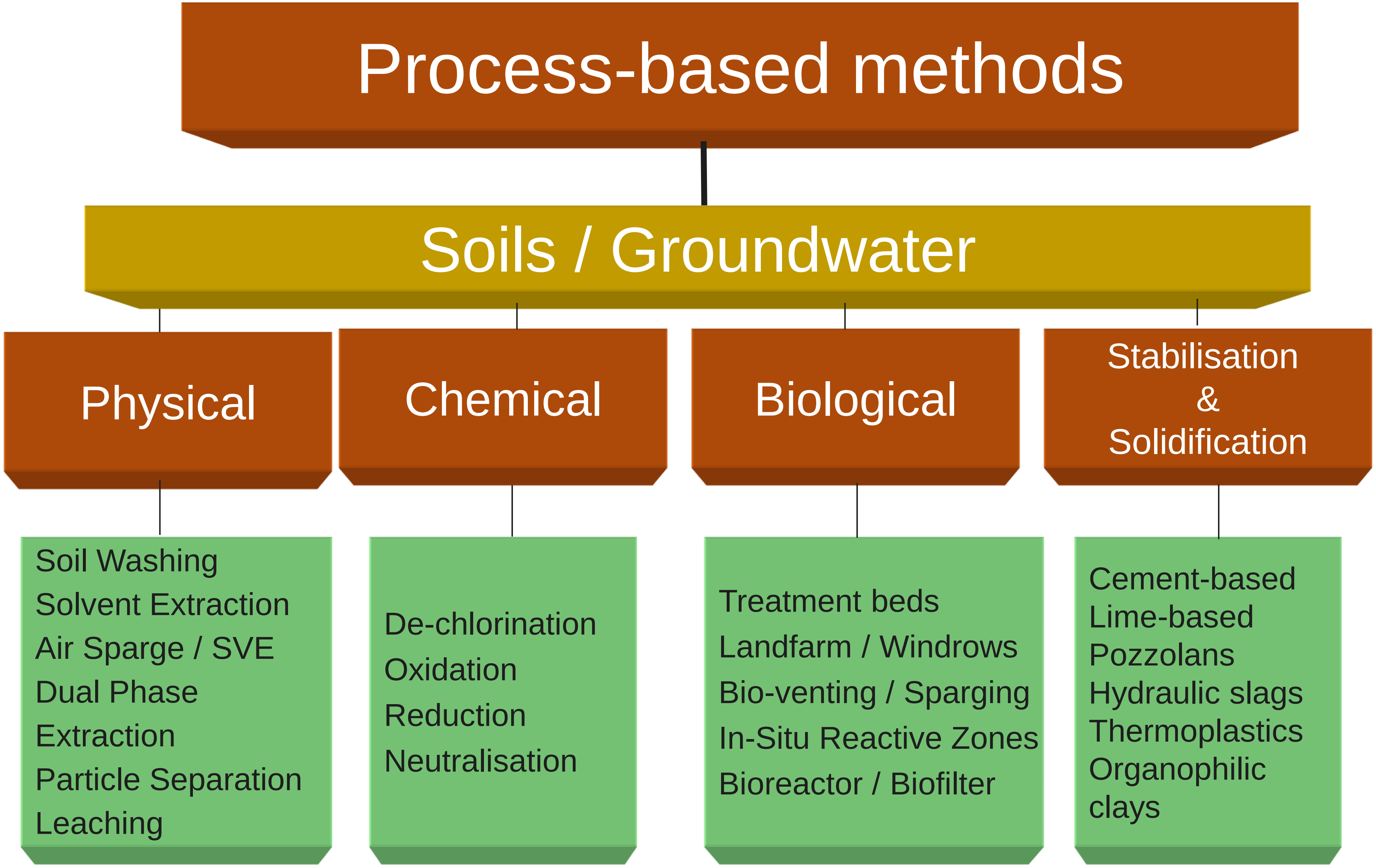

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Available In Situ Treatment Technologies for PFAS

Technology[1]	Likelihood of Success?	Rationale
Aerobic Biodegradation	Low	Biotransformation does not proceed past PFAAs
Anaerobic Biodegradation	Low	
Phytoremediation	Low	PFAAs not volatile; depth limitations
Air Sparging/Vapor Extraction	Low	PFAAs not volatile nor biodegradable
In-Situ Thermal Treatment	Low	Required temperature economically impractical; ex-situ waste management
Groundwater Extraction and Ex-Situ Treatment*	High	Presumptive remedy for PFAS to-date, focus of this discussion; ex-situ waste management
Chemical Oxidation/Reduction	Moderate	Bench-tests confirm; field evidence pending
Monitored Natural Attenuation	Low	PFAAs do not biodegrade
Permeable Reactive Barriers	High	Apply ex-situ sorption technologies with a funnel & gate; change outs required

[1]Limited to typical in-situ groundwater treatment technologies (other soil focused technologies like excavation and stabilization may be applicable for soils)

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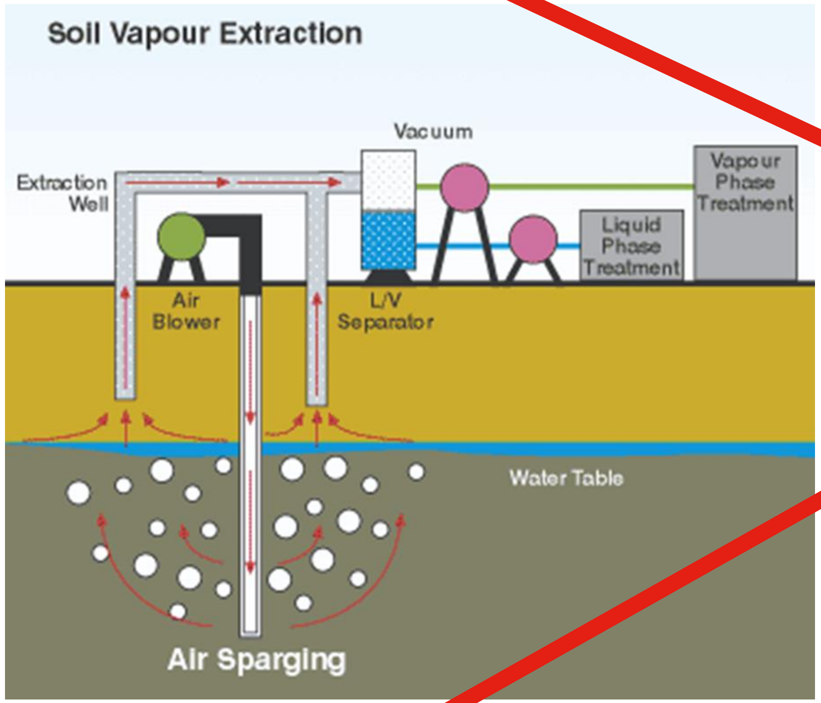
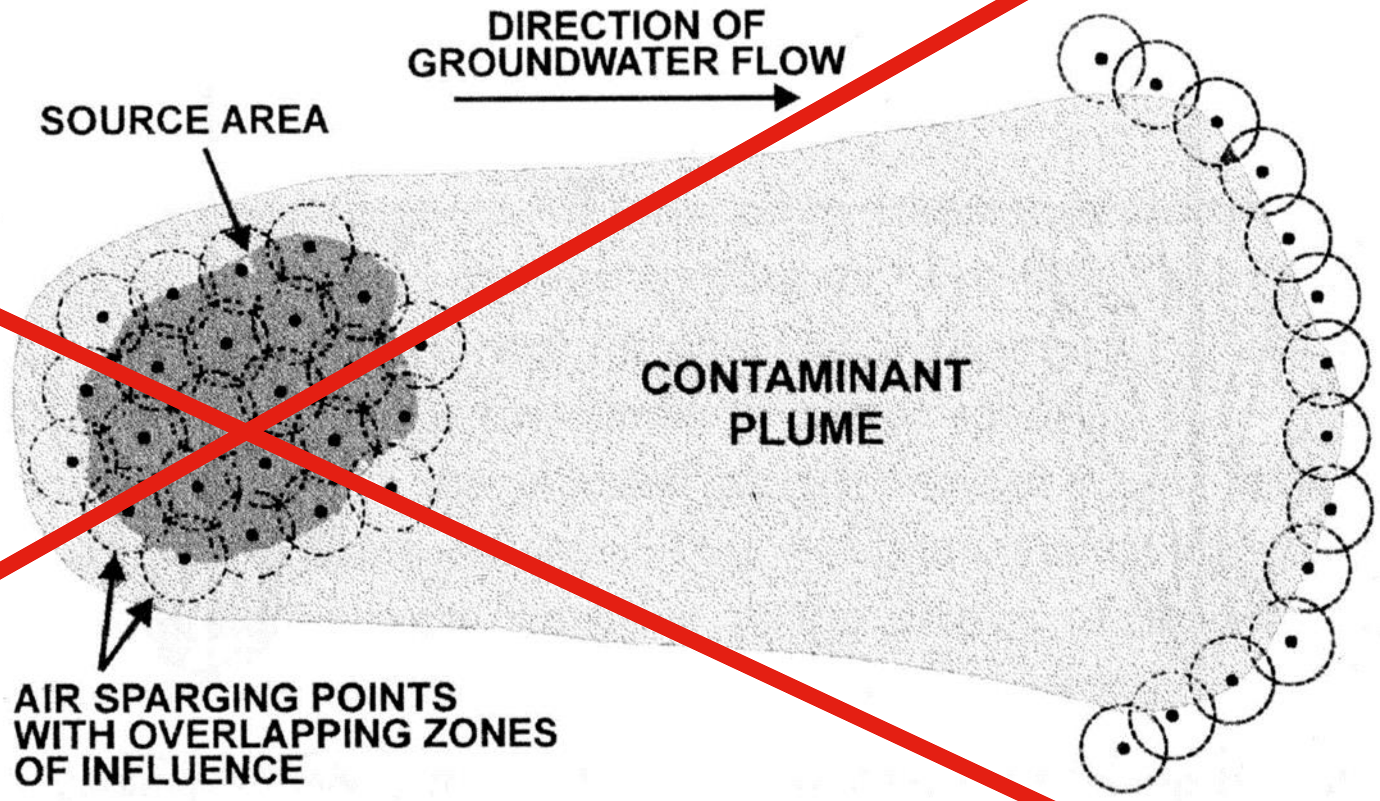
Air Sparge





Air sparging point locations in a source area and in a curtain configuration.

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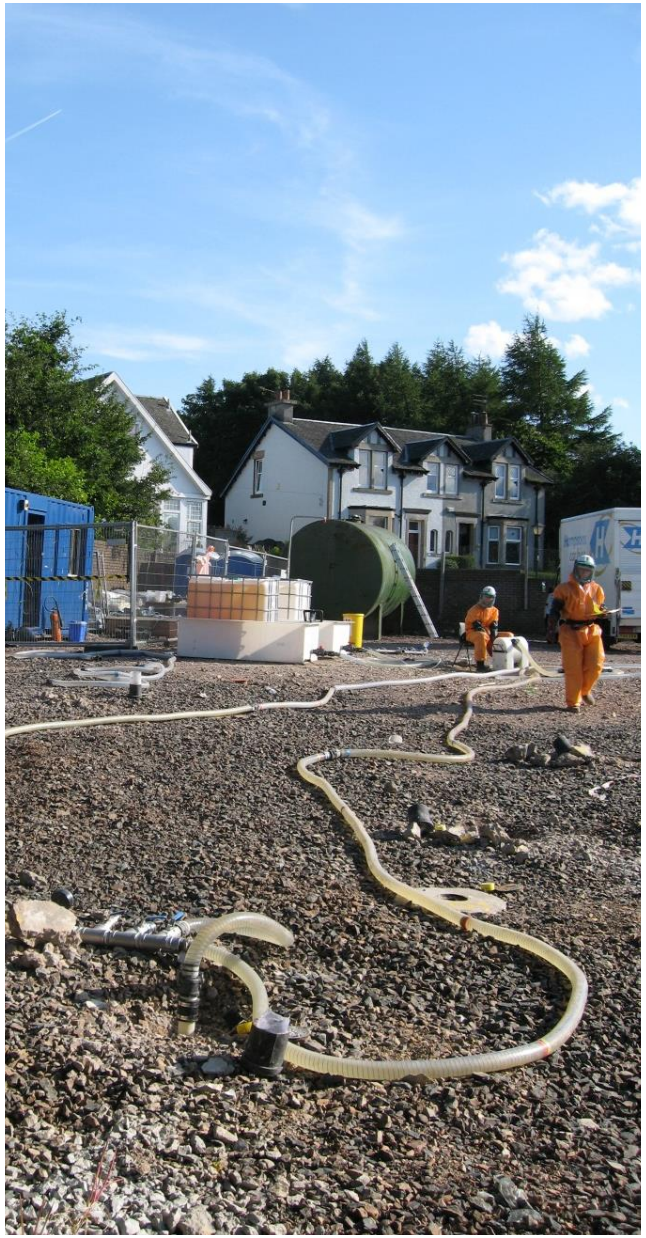
ISCO

- Standard oxidation methods make more PFCs
- More promise with PFCAs vs PFSAs but need very low pH
- TOP assay in the ground
- Potential to make more mobile PCS from precursors
- Likely also need hydraulic containment to capture breakdown products



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Soils

- Thermal desorption at (400-500 C) potentially followed by (1) off gas treatment at 900-100C
- Incineration –mobile incinerators could be sourced which run at 1,100C
- Excavation and disposal at landfill
- Soil Washing –used commercially for PFOS/PFOA in Europe, will work better on sands/gravels vs silts/clays and maybe much less effective if/when precursors are considered.
- Ex-Situ / In-Situ Smouldering –add a combustible oil to the soil and ignite, then control rate of flame front dispersion with blower –temperatures achieved?
- Stabilisation –proprietary blends of GAC/Zeolites/Clay being applied, organoclays looking better
- eBeam –firing an electron bean at impacted material, still very much experimental
- Capping / encapsulation –often used commercially as cost effective and pragmatic

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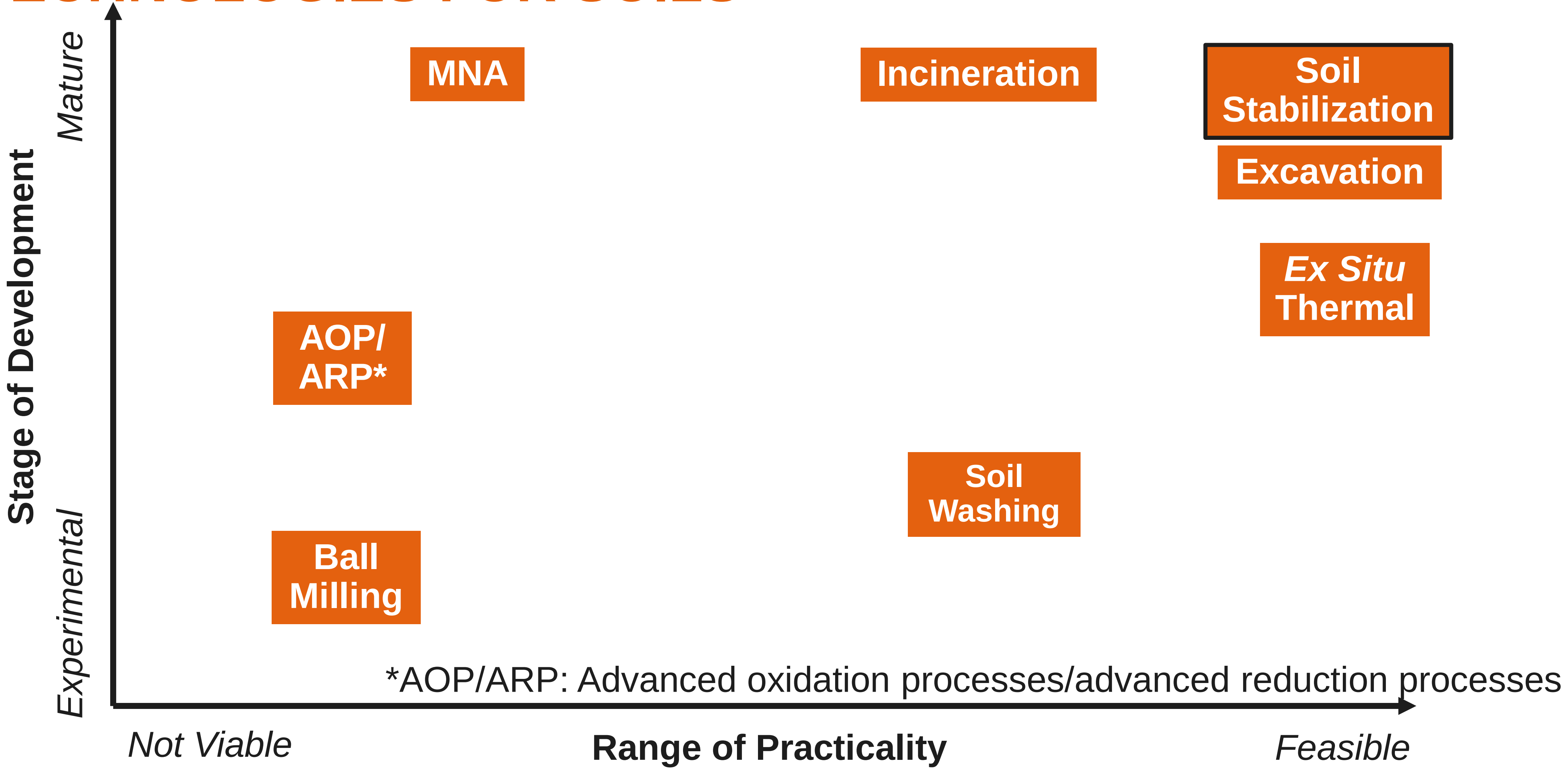
DEVELOPMENT AND PRACTICALITY: PFAS TREATMENT TECHNOLOGIES FOR SOILS



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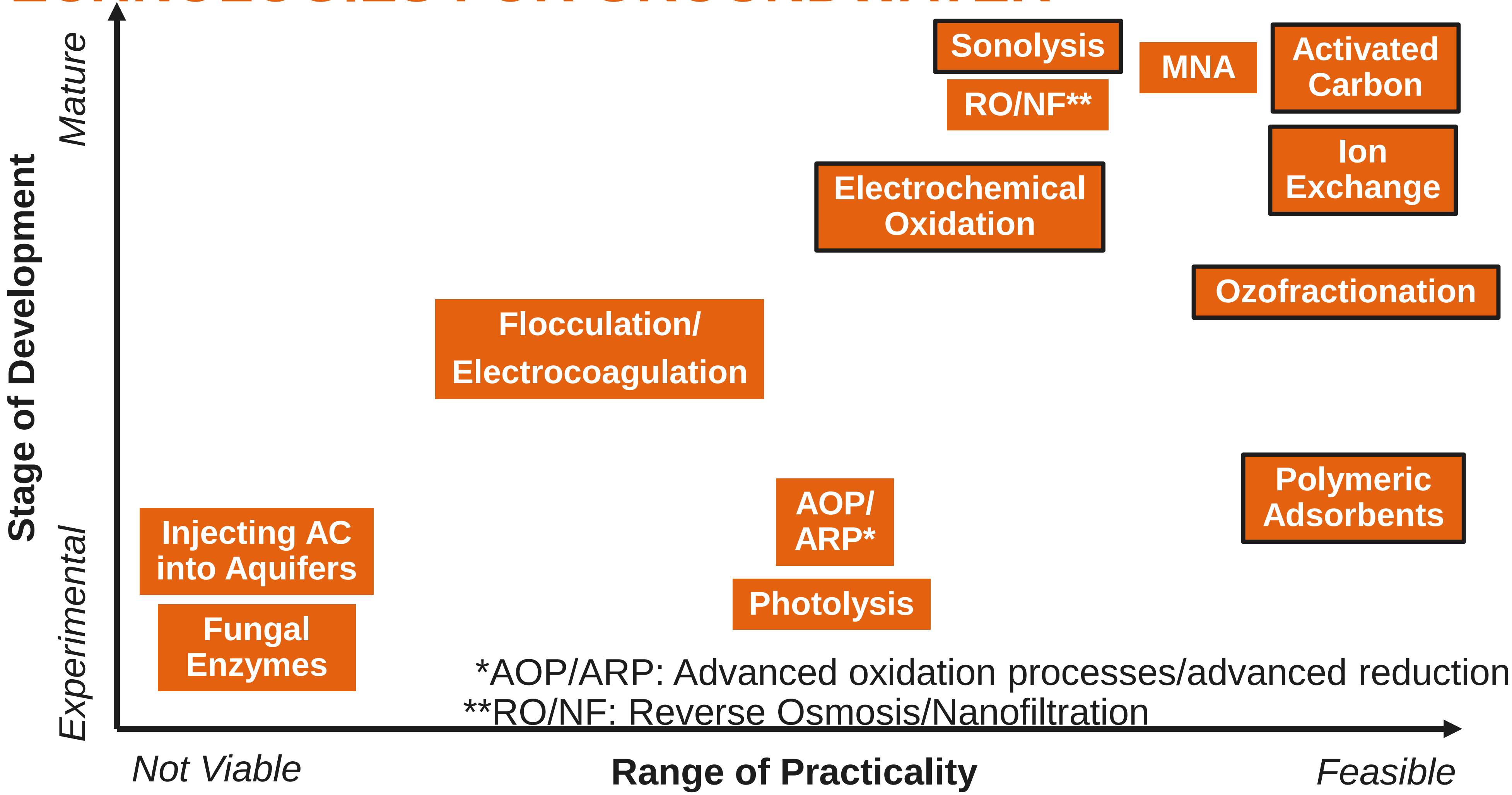
DEVELOPMENT AND PRACTICALITY: PFAS TREATMENT TECHNOLOGIES FOR GROUNDWATER



*AOP/ARP: Advanced oxidation processes/advanced reduction processes
**RO/NF: Reverse Osmosis/Nanofiltration

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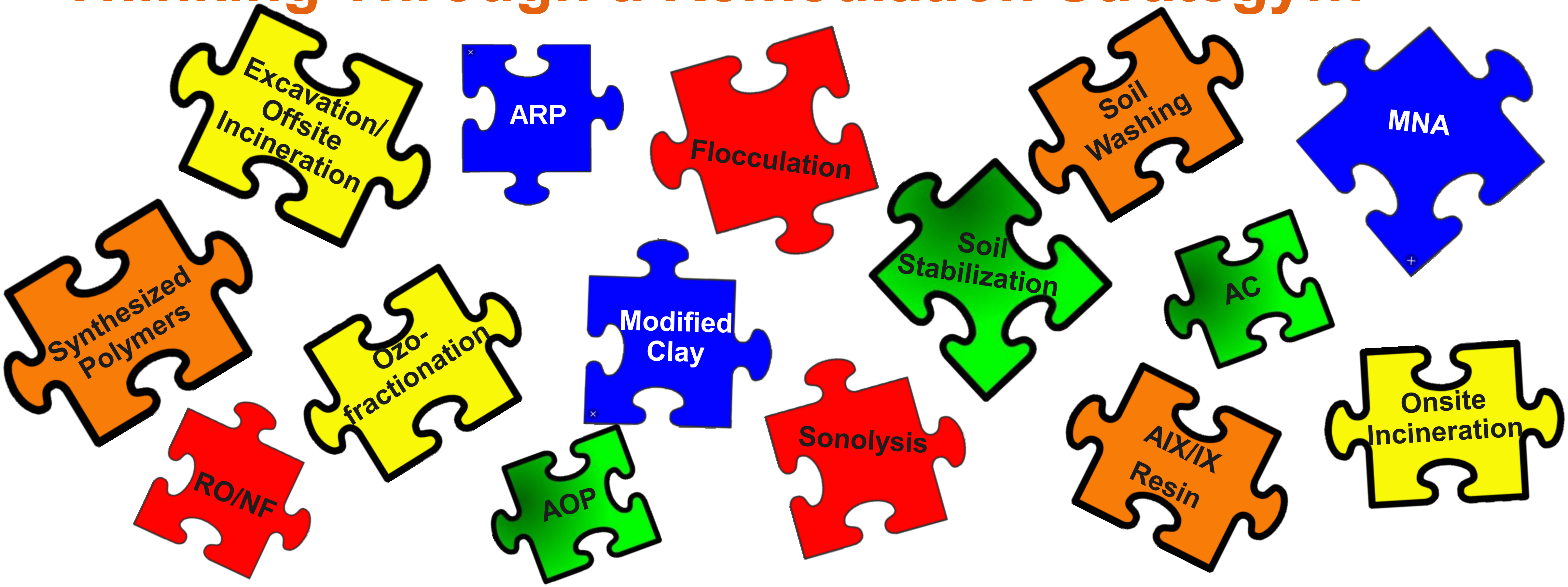
Thinking Through a Remediation Strategy…



No "silver bullet" for PFAS remediation; treatment train is current state of the practice

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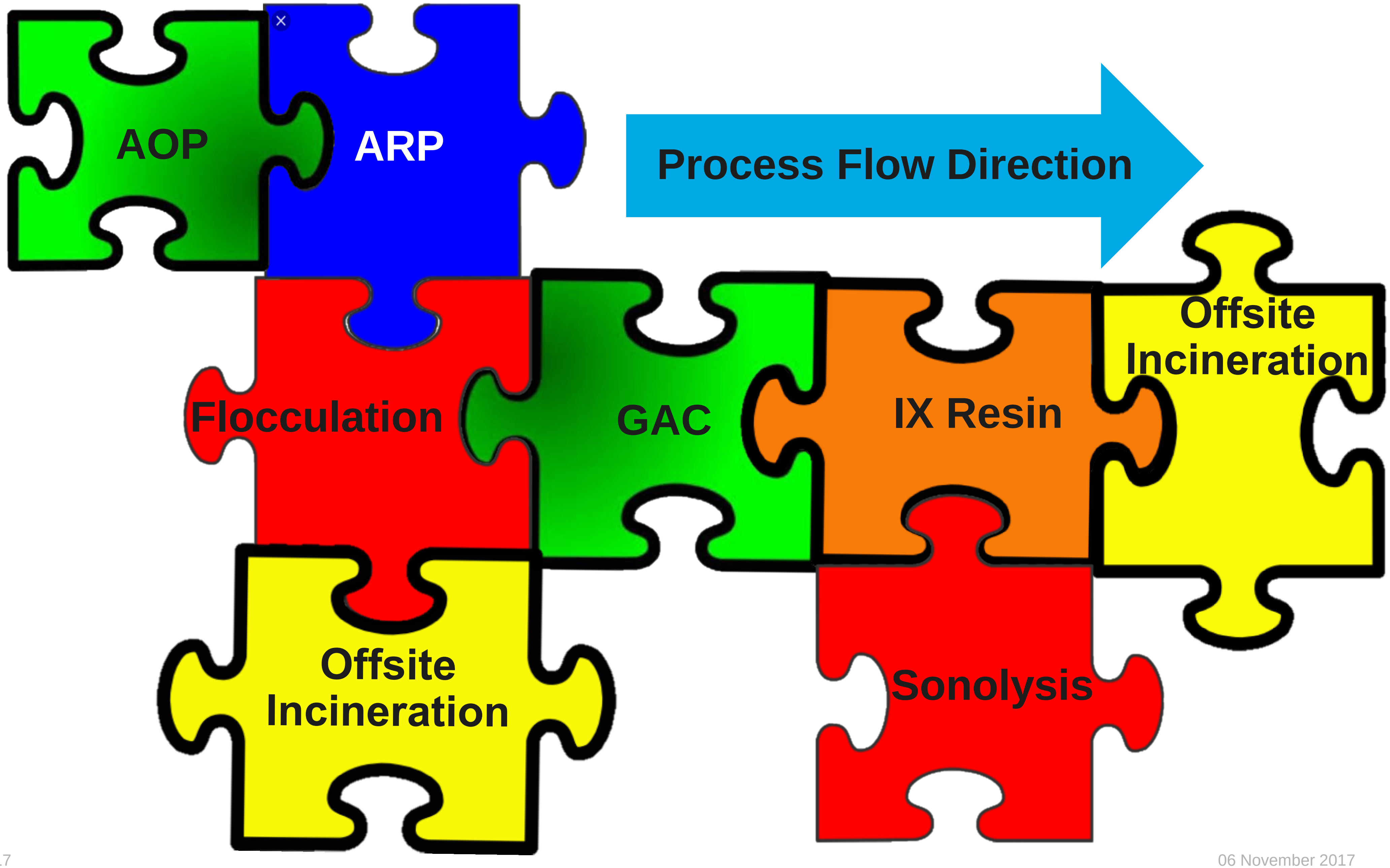
AOP
ARP
Process Flow Direction
Flocculation
GAC
IX Resin
Offsite Incineration
Offsite Incineration
Sonolysis

ADSORPTION/
SEPARATION

FIXATION

DESTRUCTION

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Phytoremediation & Wetlands

- Plumlee (2008) looking at an established wetland showed **no significant reduction in PFAS**
- Studies on food crops and soil sorption do indicate active mechanisms for uptake/sorption; short chains concentrate in fruits, long chains concentrate in root and shoots
- final destination of PFAS in plants (harvested or return to soil?)

Table 2
Perfluorochemicals (ng/l) in reclaimed wastewater from four California treatment plants and in consecutive stages of a constructed wetland for wastewater treatment and wildlife habitat

Sample	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	N-EtFOSAA	Total PFCs
Reclaimed wastewater											
WWTP 1[a]	24	38	9.0	8.8	36	n.d. (<10)	11	11	2.8	11	150
WWTP 2[b]	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470
WWTP 3[c]	6.5	20	n.d. (<2)	21	190	14	11	n.d. (<4)	4.8	5.5	270
WWTP 4[d]	8.0	42	3.3	5.6	12	n.d. (<10)	n.d.	n.d. (<4)	2.1	12	90
Constructed wetland using primary treated wastewater											
Oxidation pond influent	3.4	23	36	n.d. (<4)	14	9.1	3.4	n.d. (<4)	8.8	48	150
Oxidation pond effluent	3.2	21	23	n.d. (<4)	13	7.8	n.d. (<2)	n.d. (<4)	6.9	69	140
Treatment marsh effluent	3.0	25	29	n.d. (<4)	12	5.4	n.d. (<2)	n.d. (<4)	6.9	59	140
Enhancement marsh 1 influent	3.2	23	14	n.d. (<4)	11	3.3	n.d. (<2)	n.d. (<4)	5.3	40	100
Enhancement marsh 1 effluent	3.3	19	10	16	9.1	3.0	n.d. (<2)	n.d. (<4)	4.5	41	110
Enhancement marsh 3 effluent	3.2	29	36	n.d. (<4)	11	3.5	n.d. (<2)	n.d. (<4)	7.4	85	170

Values are the mean of duplicate samples (mean percent difference between duplicate samples was 21%).
[a] Tertiary treatment via dual media filtration and chlorination, followed by polymer treatment and repeated filtration for reclaimed wastewater.
[b] Tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater.
[c] Tertiary treatment via dual media filtration and chlorination.
[d] Tertiary treatment via fixed growth reactor (ammonia removal), flocculation, dual media filtration, and chlorination, followed by additional flocculation, dual media filtration, and chlorination for reclaimed wastewater.

Perfluorochemicals in water reuse. Plumlee et al. 2008
Chemosphere. doi:10.1016/j.chemosphere.2008.04.057;

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Alternative water treatment options

Compound	M.W. (g/mol)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO_4, O_3, ClO_2, CLM, UV-AOP)	Anion Exchange (select resins tested)	**Granular Activated Carbon**	**Nano Filtration**	**Reverse Osmosis**
PFBA	214	assumed	assumed						
PFPeA	264								
PFHxA	314								
PFHpA	364								
PFOA	**414**								
PFNA	464					assumed	assumed		
PFDA	514					assumed	assumed		
PFBS	300								
PFHxS	400								
PFOS	**500**								
FOSA	499						assumed		assumed
N-MeFOSAA	571	assumed				assumed	assumed	assumed	
N-EtFOSAA	585					assumed	assumed	assumed	

Conventional Treatment

Specialized Treatment

> 90% removal

> 10%, < 90% removal

< 10% removal

unknown

Dickenson and Higgins, 2016. Treatment mitigation strategies for poly- and perfluoralkyl substances, Water Research Foundation

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Granular Activated Carbon (GAC)

Applicability:

- GAC can effectively remove PFOS/PFOA from water (>90%).
- Type of GAC: bituminous outperforming coconut, also consider powdere
- Microporous GAC indicated to be most effective

Benefits:

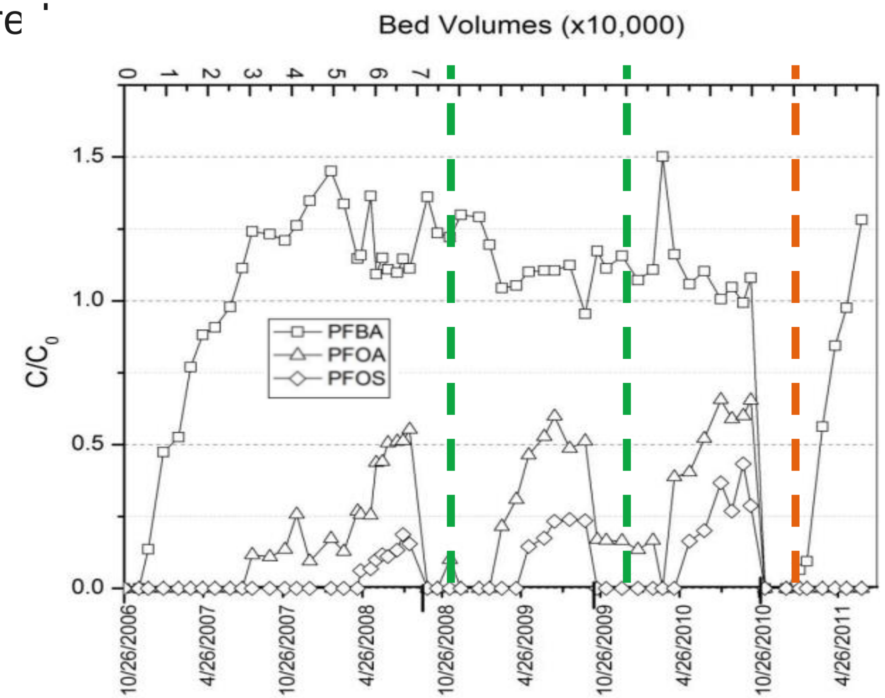
- Manages low concentrations; low flow rates; compatible geochemistry (low natural organics, low hardness, low PFAS, etc.).
- Easily saleable, rapid deployment.

Limitations:

- 80x less sorptive capacity for PFOS vs. BTEX.
- Effectiveness decreases as PFAA chain length decreases, C4 poor.
- Long term O&M cost.
- Little know about effectiveness at removing precoursors

Deployment:

- Competition with natural organics, precursors, and other contaminants will effect performance.
- Reactivated GAC can remove PFOS/PFOA.



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Dickenson and Higgins, 2016

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Environmental Science & Technology
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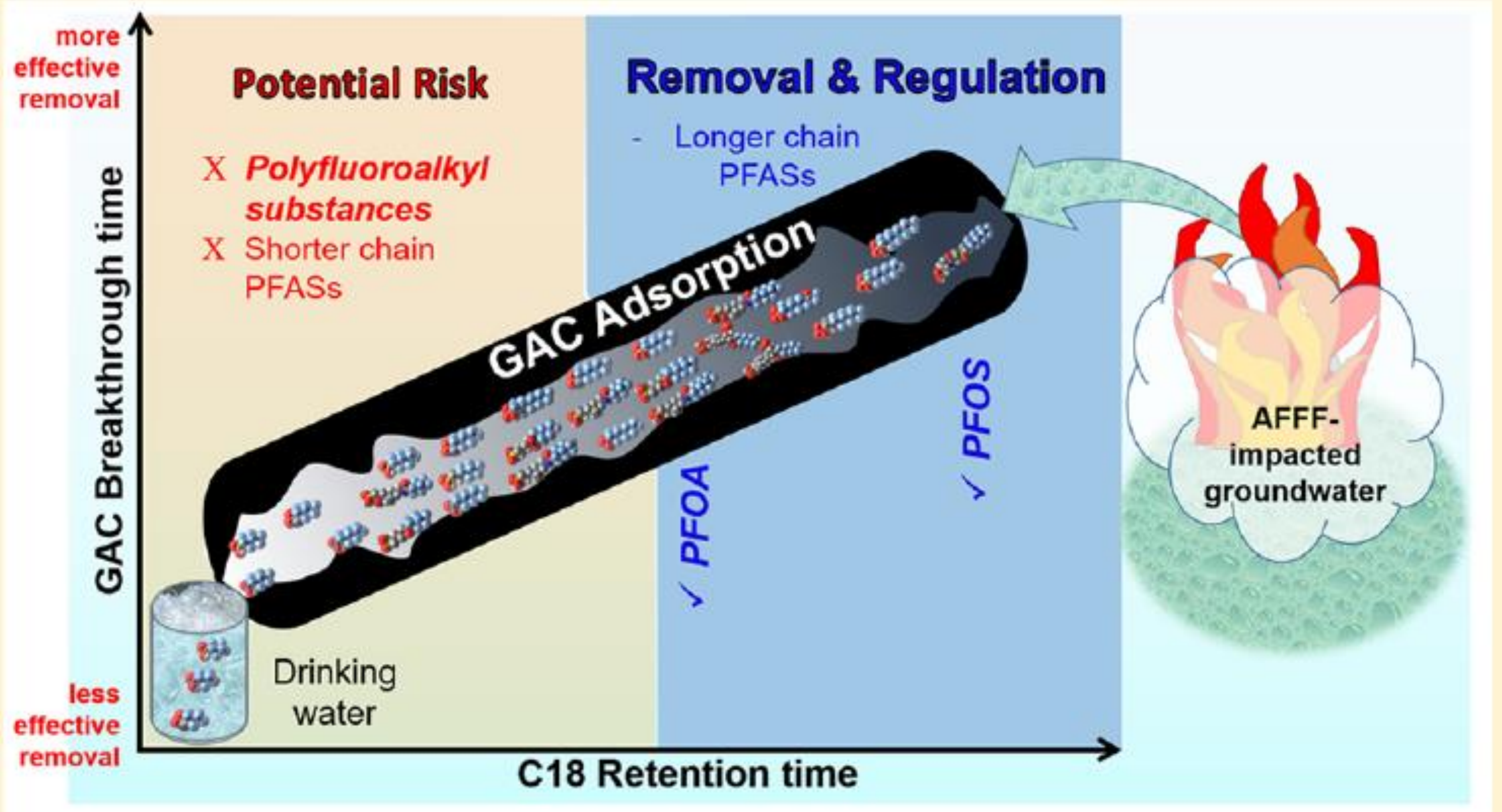
Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon

Xin Xiao,[†,‡,§] Bridget A. Ulrich,[‡] Baoliang Chen,[†,§] and Christopher P. Higgins*[,‡]



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Engineering GAC for PFAS

- Influent Flow Rate
- Empty Bed Contact Time
- **Carbon Type**
- Pretreatment Considerations

- A larger percentage of medium-sized pores (mesopores) as compared to bituminous GAC may perform well for PFAS removal
- Column tests with >3 mg/L TOC suggest sub-bituminous GAC performed as well as a bituminous carbon (table)
- Alternative GAC may offer cost savings: sub-bituminous and lignite-based GACs are less dense than bituminous and coconut carbons

GAC Type	BV to Initial PFOA Breakthrough	BV to Initial PFOS Breakthrough
Bituminous	12,000	12,000
Sub-bituminous	12,000	19,000

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ACTIVATED CARBON (GRANULAR OR POWDERED)

Surface Water	Ground Water	Point Of Entry (POE) Systems
✓	✓	✓

Applicability:

- AC can effectively remove PFOA/PFOS from water (>90%); 7 to 15 empty bed contact time (EBCT).
- Reactivation viable, improves sustainability, reduce cost ~15%, may also improve removal performance.

Benefits:

- Manages low PFOA/PFOS concentrations; low flow rates.
- Well understood, community friendly, rapid deployment, “de facto IRM.”

Limitations:

- Effectiveness decreases as PFAA chain length decreases; questionable removal of precursors. May be managed with longer EBCT?
- Competition with natural organic materials (NOM)/total organic carbon (TOC).
- Perpetual for the foreseeable future until destructive technologies develop (focus on **optimization**).

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OPTIMIZING ACTIVATED CARBON (GRANULAR OR POWDERED)

Understand the commercially available AC:

- Bituminous, sub-bituminous, anthracite, lignite, coconut shell
- PFAS specific iodine number paradigm shift (mesoporosity favorable over microporosity)
- Apparent density (**Table 1**)

GAC Type	BV to Initial PFOA Breakthrough	BV to Initial PFOS Breakthrough
Bituminous	12,000	12,000
Sub-bituminous	12,000	19,000

Table 1: Comparative PFOA/PFOS breakthrough at >3 mg/L TOC and ~150 ng/L PFOS and 25 ng/L PFOA influent concentrations

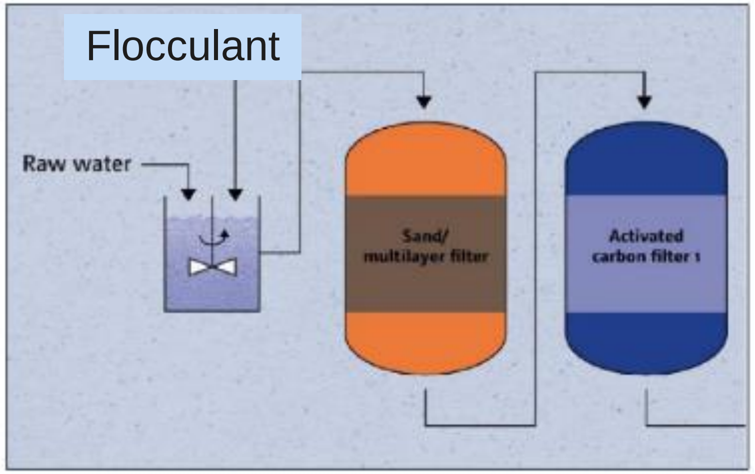
Natural organic matter (NOM), measured as total organic carbon (TOC), is found in natural waters (<0.5 to >3 mg/L).

- TOC can outcompete PFOA/PFOS for adsorption site/pore obstruction (**Table 2**).
- TOC becomes less sorptive as pH increases; slight pH adjustments pre-AC may improve efficiency.

Influent PFOA Conc. (ng/L)	TOC (mg/L)	BV to Initial PFOA Breakthrough
20	0.3	>100,000
25	3.3	25,000

Table 2: Comparative influence of TOC on PFOA breakthrough

Protecting GAC

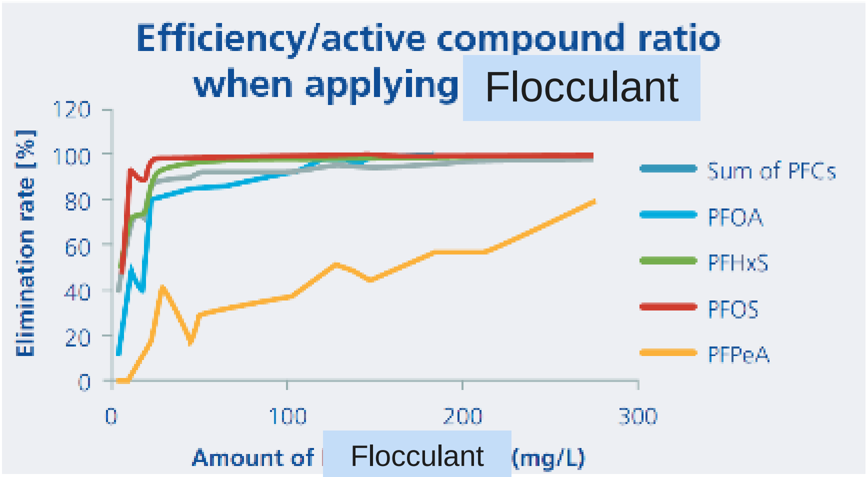


Applicability:

- Flocculation/precipitation can remove PFOS/PFOA from water (>20,000 ng/L).

Sweet Spots:

- High influent concentrations to a GETS before GAC, AIX, RO, or NF.



Limitations:

- Precipitated flocculant becomes a sludge that requires disposal (likely incineration/landfill?).
- Will not achieve 70 ng/L on its own.
- Rate of flocculant formation is influenced by geochemistry; flocculation/precipitation rates may be difficult to manage at higher flow rate systems.

Deployment:

- Treatment train – initial reduction of elevated concentrations.
- Pre-design bench-scale work required ahead of dosing design calculations.

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ANION/ION EXCHANGE

Applicability:

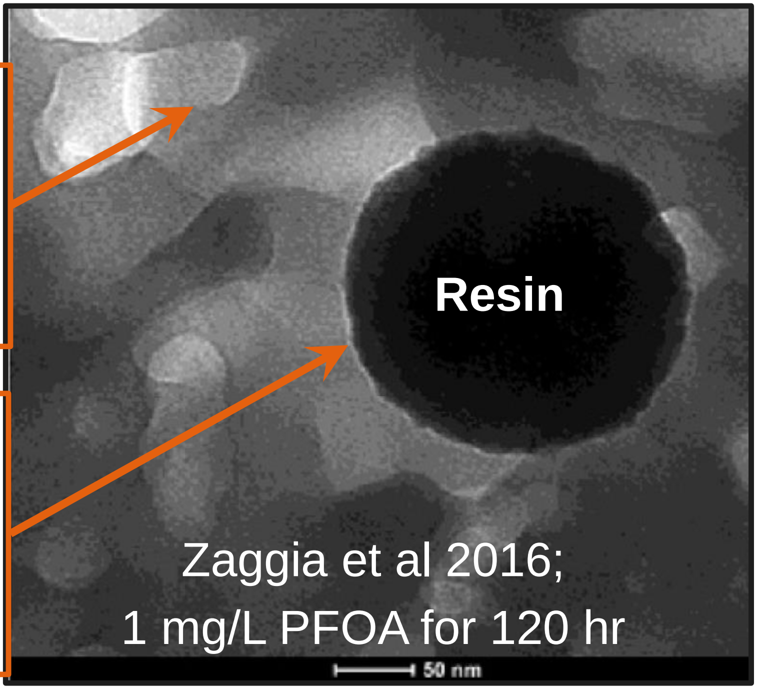
- AIX can effectively remove PFAAs from water with effectiveness ranging from 10% to >90%.
- Reactivation methods available, though high throughputs may justify single use.

Benefits:

- Engineered resins (variable functional groups on the surface of polystyrene or polyacrylic resins) enable enhanced selectivity.
- Smaller equipment footprints, lower EBCT than AC (3 min versus 7 to 15 min).

Hydrophobic attraction may create aggregates between resins

Electrostatic adsorption as a monolayer along the surface of the resin



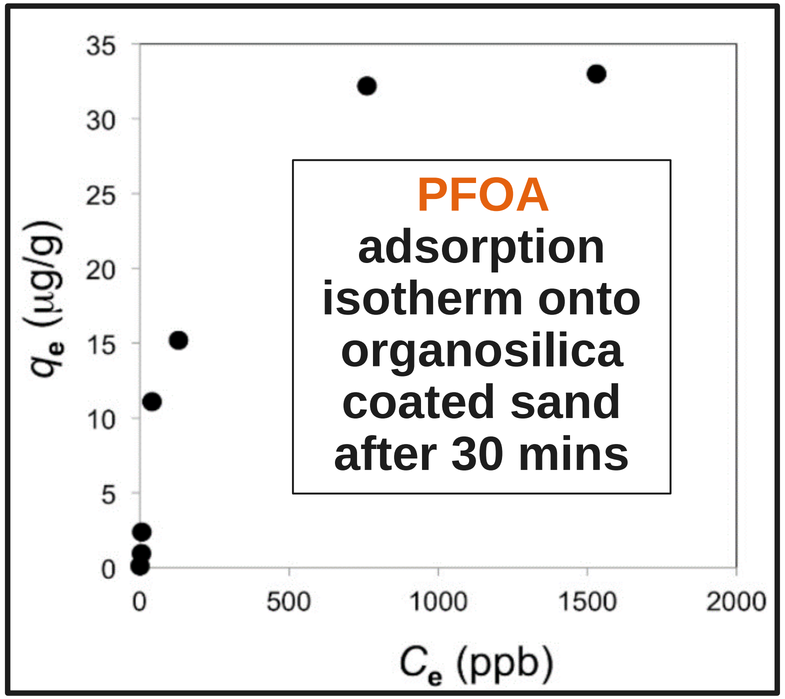
Zaggia et al 2016;
1 mg/L PFOA for 120 hr

- Recent field-test data suggests enhanced AC performance with AIX polish and demonstrated greater removal of PFHpA, PFNA, PFHxS, and PFBS.

Limitations:

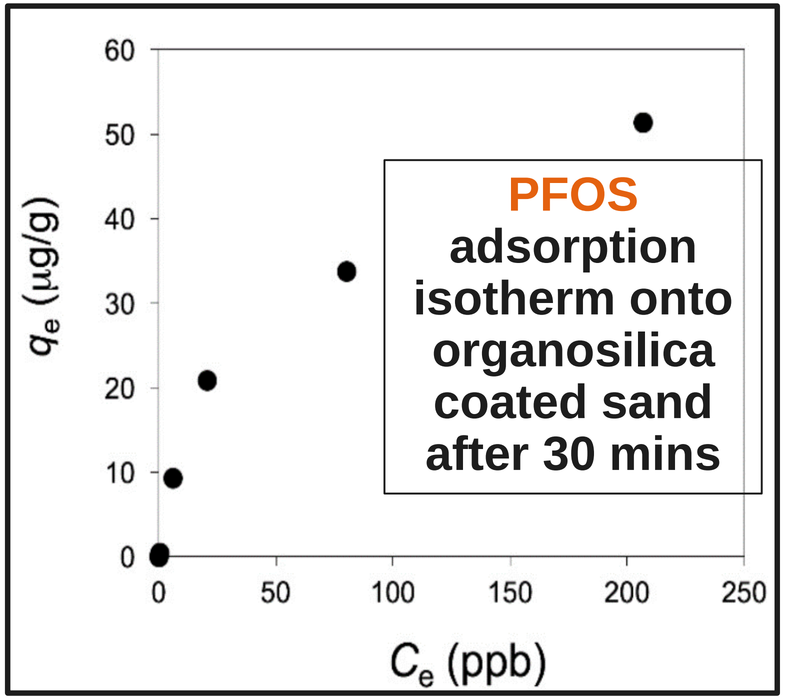
- Sensitive to site-specific geochemistry; methanol/brine reactivation may be required; comparative assessment of engineered resins challenged by inconsistent data reporting in the literature.

New Engineered Sorbents!



Fine Sand

Organosilica Coated Sand



- Crosslinked alkoxysilicanes forming a microporous matrix
- Adsorbs organic compounds (expands 3-5 times volume)
- Effective for log $K_{OW} > 2.5$
- Synthesized polymers could use fluorinated chains to enhanced adsorption

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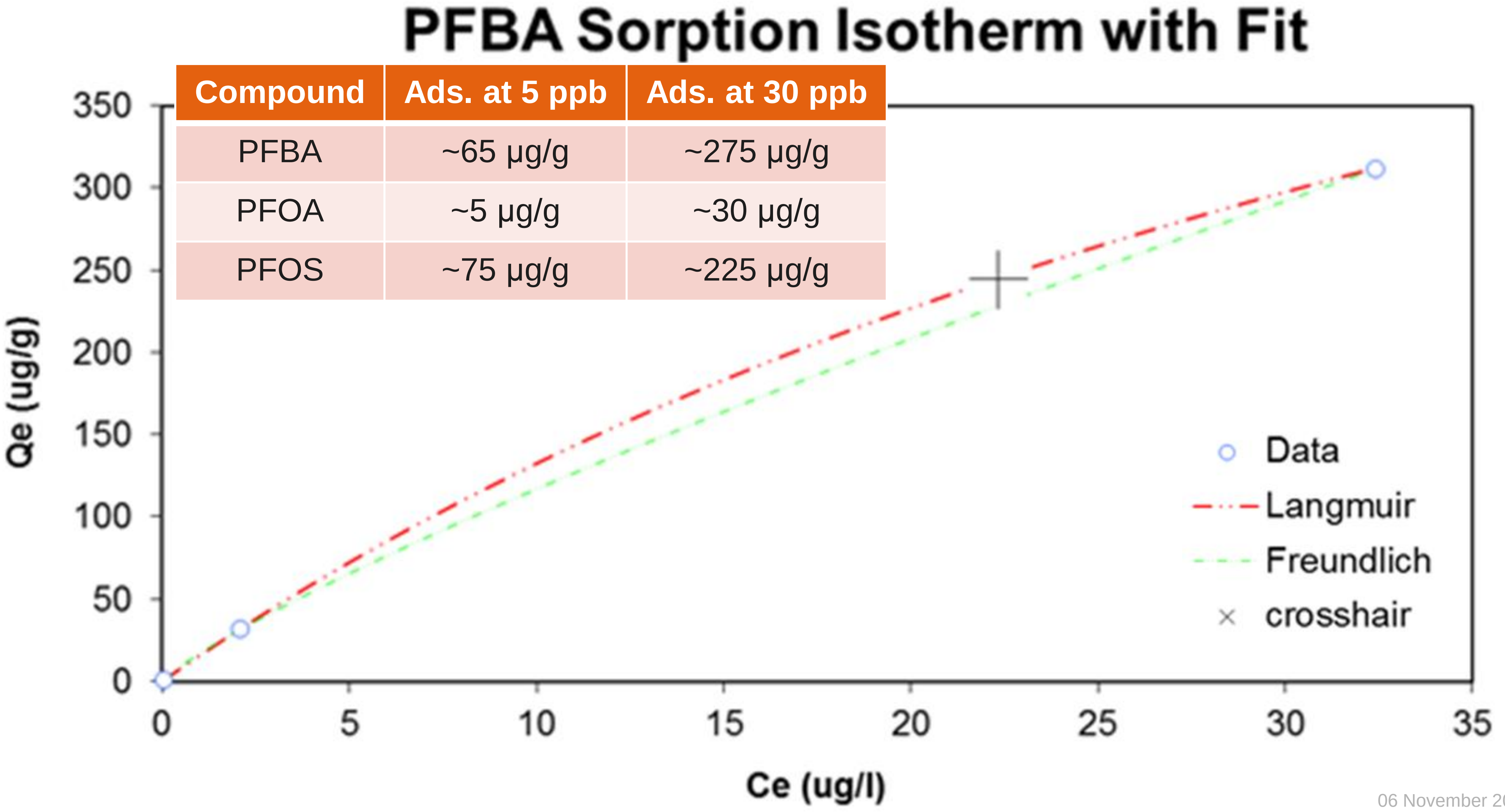
…With Removal of Short Chain?



Compound	Ads. at 5 ppb	Ads. at 30 ppb
PFBA	~65 µg/g	~275 µg/g
PFOA	~5 µg/g	~30 µg/g
PFOS	~75 µg/g	~225 µg/g

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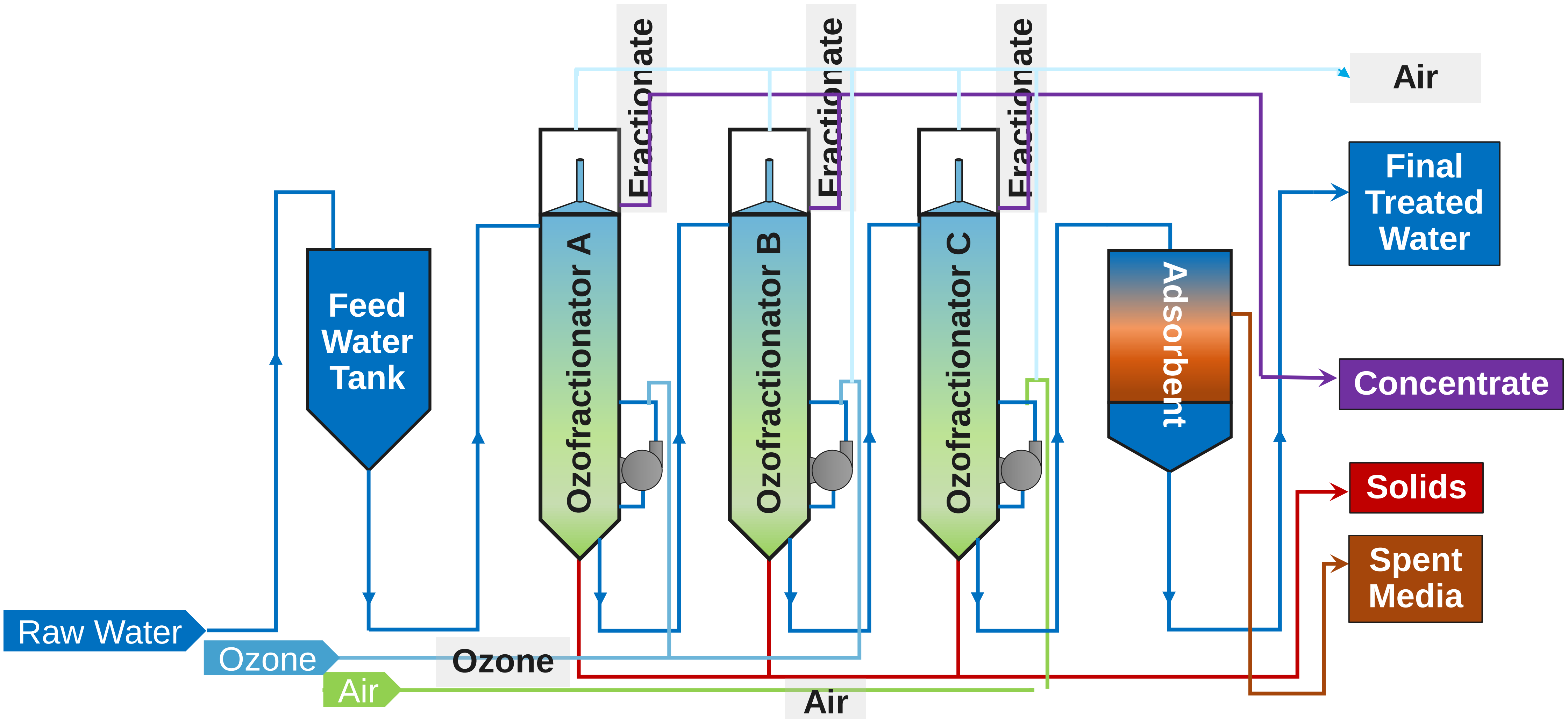
Swedish Chemicals Agency

Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014

PM 6/15

Tentatively identified PFAS as a main ingredient is 6:2 FTSAS (fluorotelomermercaptoalkylamido sulfonate).

Ozofractionation - Concept



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Ozofractionation – Case Study

Large volume high COD, high PFAS impacted wastewater

- ~3.6 million gallons of water
- Total [PFAS] ~ 3,950 µg/L; targeted discharge [PFAS] = <1 µg/L
- Laboratory analysis includes total oxidizable precursor (TOP) assay per country-specific regulations

Treatment train operation selected

- Ozofractionation with engineered polish
- Polish necessary for low discharge limit
- Foam concentrate to be thermally destroyed offsite

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Ozofractionation – Case Study

Ozofractionation highly effective at removing PFOS, PFOA, and C6 PFAA precursors.

Ozofractionation converted some C6 precursors to PFHxA, PFPeA – net production of these compounds

Polishing adsorption stage was effective at removing PFHxA and, to a lesser extent, PFPeA; PFBA was not detectable in these samples

Identification	Influent (µg/L)	Ozofraction % Removal	Adsorbent % Removal	Treated Water (µg/L)	Total % Removal
PFOS	2.61	98.2%	81.3%	0.009	99.7%
PFOA	1.37	97.4%	94.4%	0.002	99.9%
6:2 FtS	87.4	95.6%	89.2%	0.416	99.5%
PFPeA	2.08	-66.3%	83.4%	0.575	72.4%
PFHxA	6.91	-66.4%	99.7%	0.034	99.5%
Sum PFAS	103	78.8%	95.1%	1.07	99.0%
Total PFAS, TOPA	**3,950**	**99.6%**	**89.6%**	**1.76**	**99.96%**

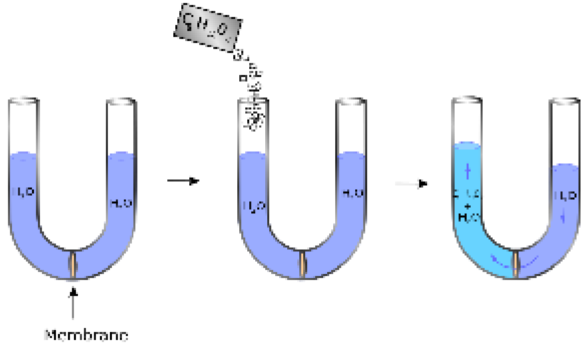
Ozofractionation and engineered polish achieve 99.96% PFAS removal, post TOP

Nanofiltration (NF) and Reverse Osmosis (RO)

Surface Water	Ground Water
✓	✓

Applicability:

- NF (0.001 µm) can remove PFAAs from water (>95%).
- RO can effectively remove PFAAs from water (>99%).
- Membranes are susceptible to fouling; pre-treatment likely required.



Benefits:

- Can be combined with GAC and pre-treatment for better overall PFAAs removal.
- Most effective technology at removing smaller chain PFAS (e.g., PFBA).

Limitations:

- Reject water must be treated before being discharged.
- High capital cost with high energy demand; susceptible to fouling (likely requires pretreatment to prevent fouling).
- RO can produce aggressive water

Deployment:

- Maintaining constant operation conditions (e.g., flux, cross-flow velocity, and recovery) independent of fouling is important.
- Natural organic matter may increase rejection at the filtration surface.

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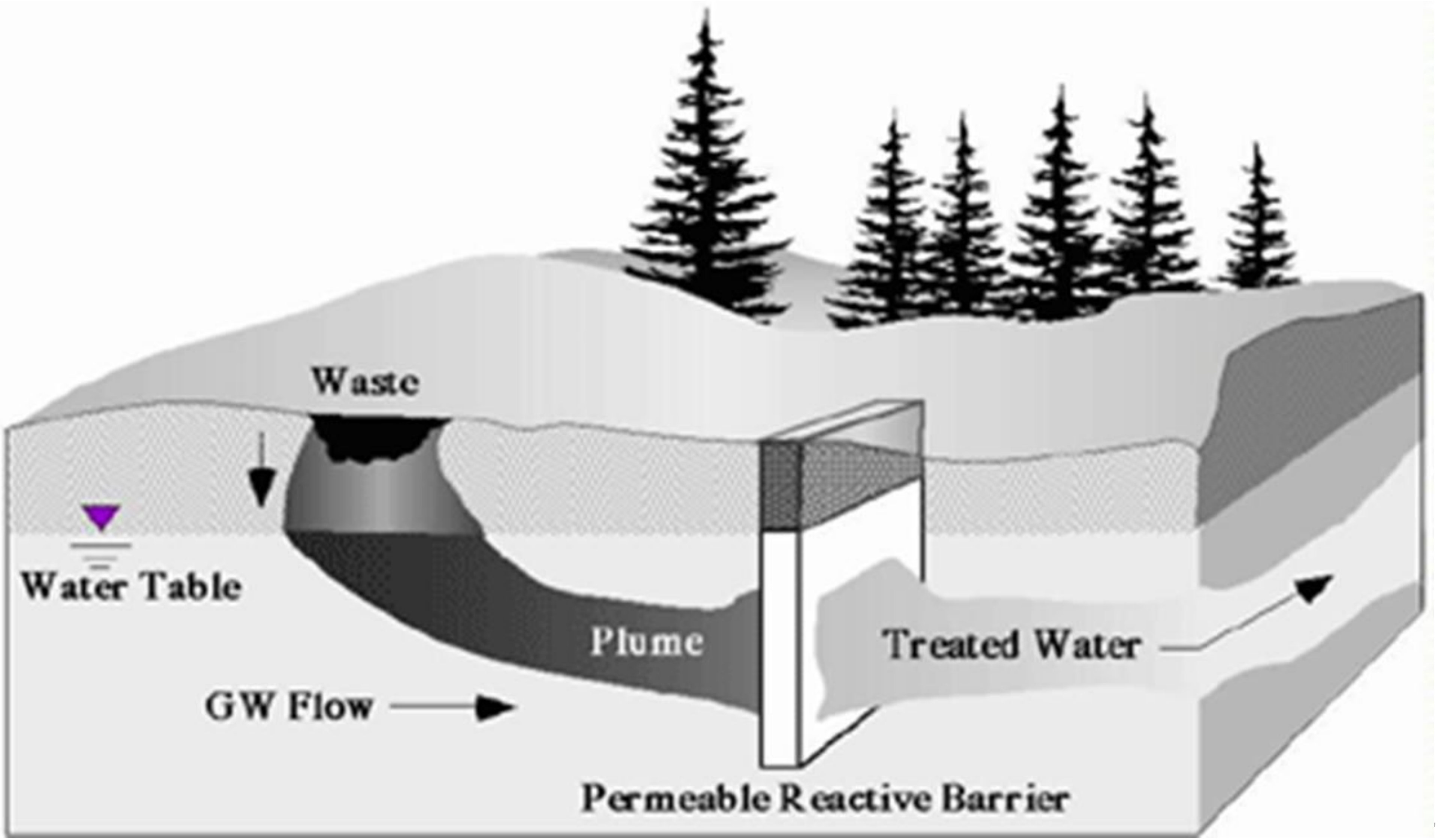
Permeable Reactive Barriers



ADSORPTION/ SEPARATION

FIXATION

DESTRUCTION

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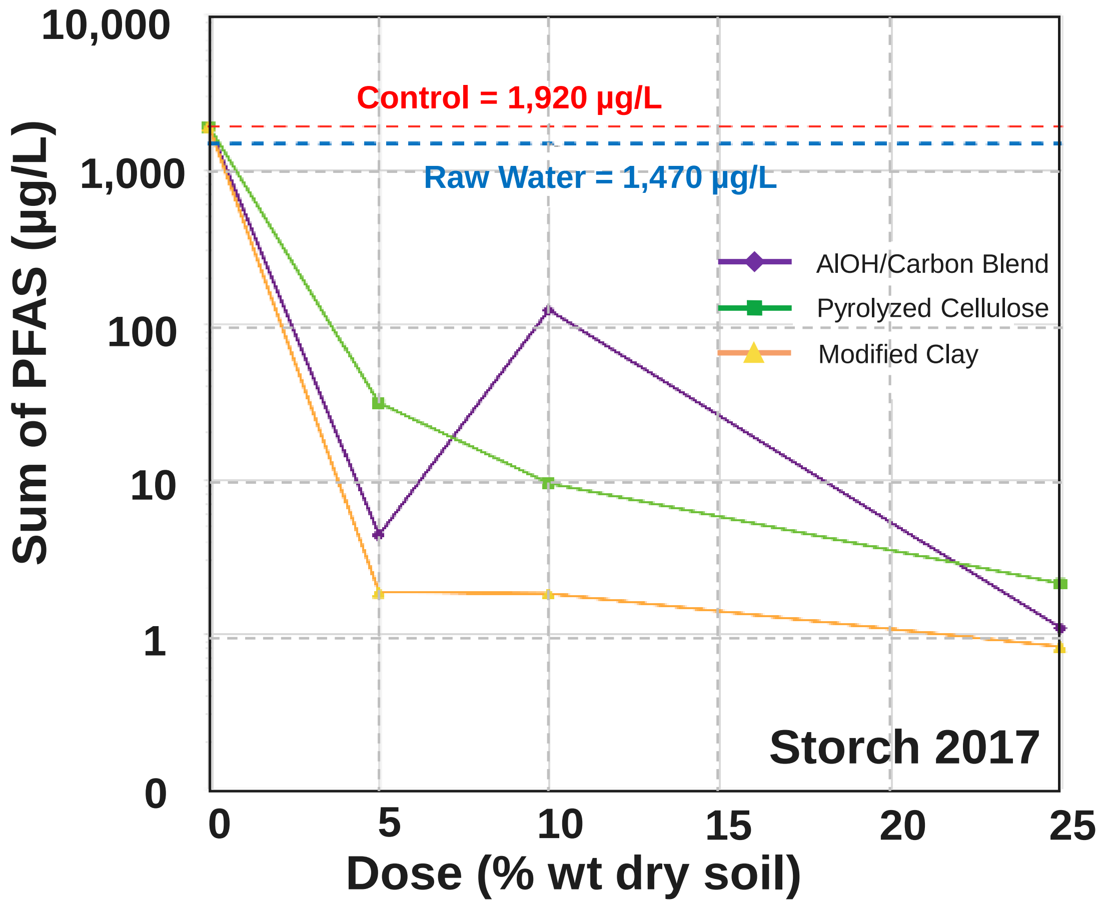
Fixation to Support *In Situ* Soil Stabilization



PFAS removal from supernatant in a soil/GW/adsorbent slurry at different % dry soil weight doses.

Adsorbents tested (left to right): aluminum hydroxide and carbon blend, clay, and pyrolyzed cellulose

Will it be effective long-term?

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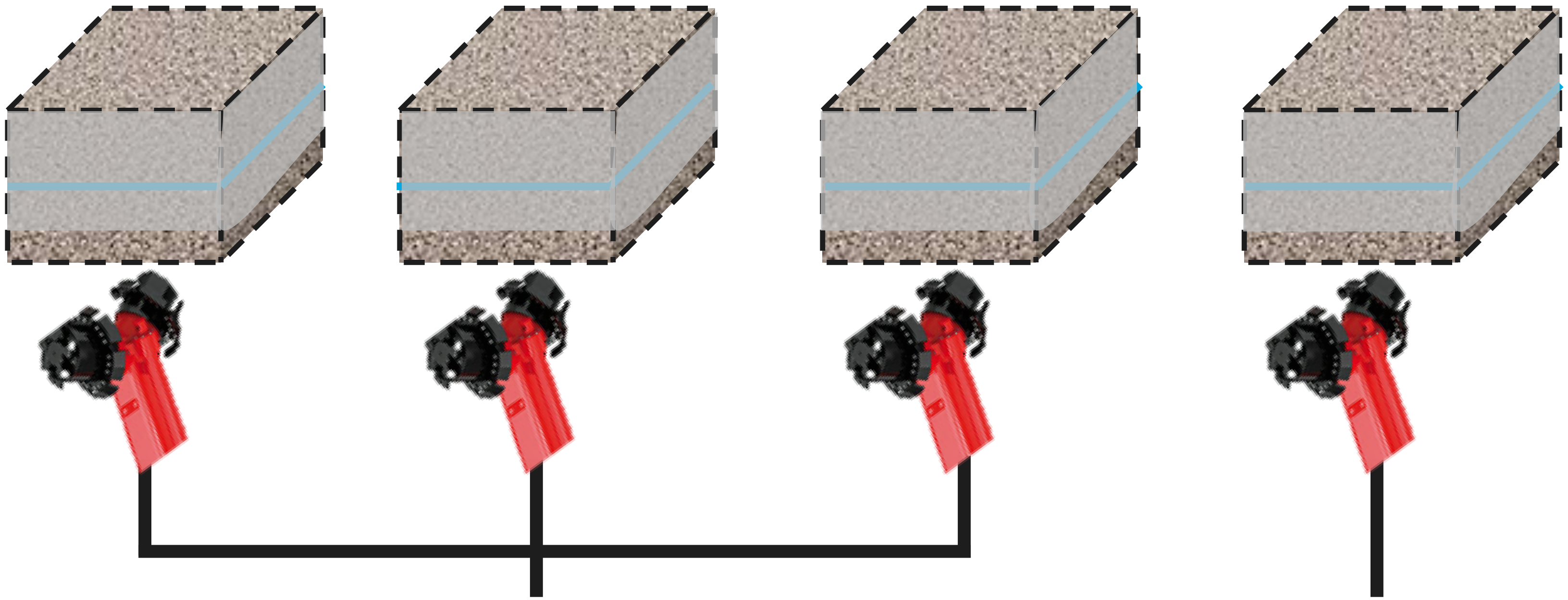
Fixation to Support *In Situ* Soil Stabilization

First ever
field-scale
time series
comparison of
fixation
permanence



Stabilizers (“fixants”) and Portland Cement

Control (Portland Cement)

DoD Funded BAA 2017

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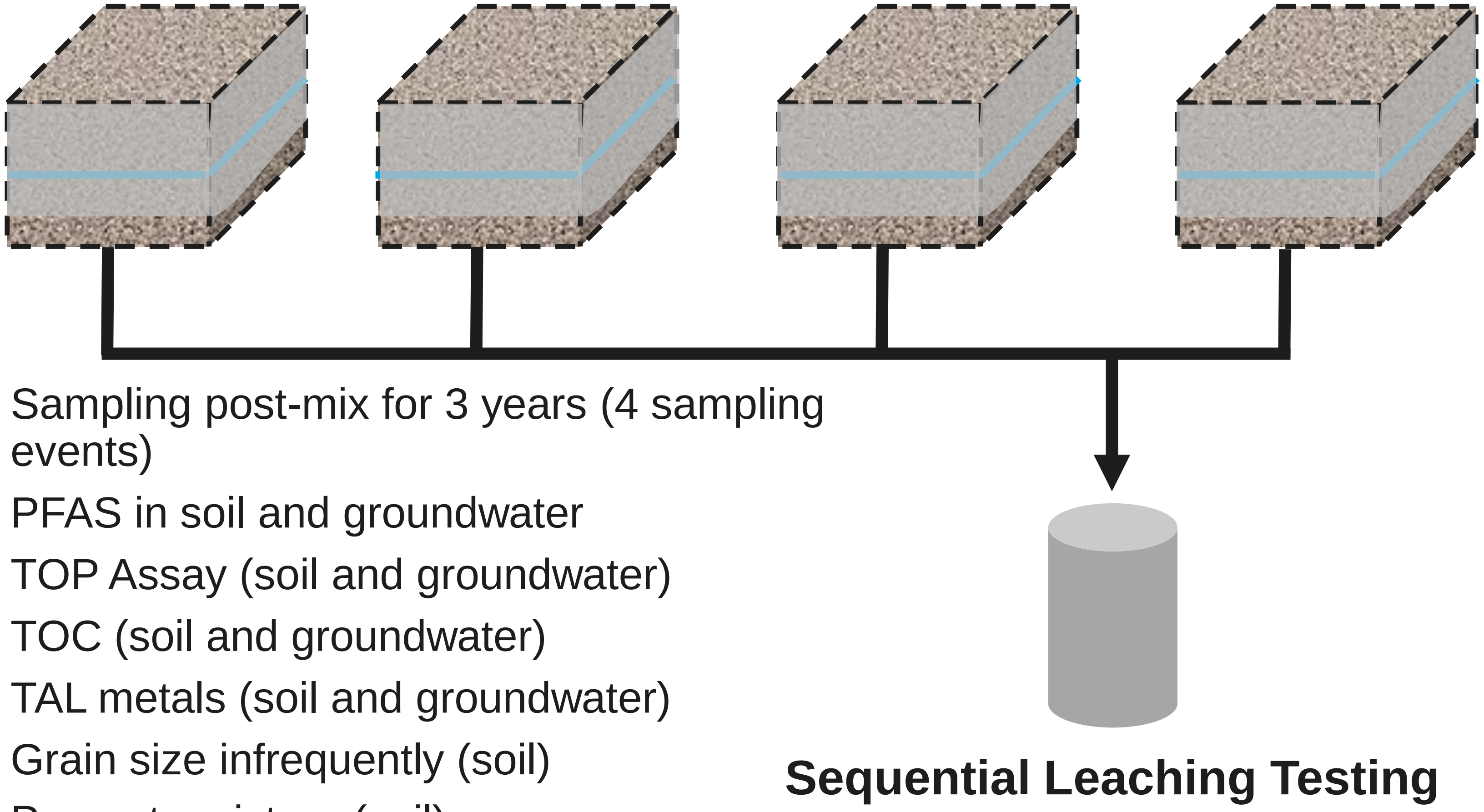
Fixation to Support *In Situ* Soil Stabilization

First ever **field-scale** time series comparison of fixation permanence



- Sampling post-mix for 3 years (4 sampling events)
- PFAS in soil and groundwater
- TOP Assay (soil and groundwater)
- TOC (soil and groundwater)
- TAL metals (soil and groundwater)
- Grain size infrequently (soil)
- Percent moisture (soil)
- Major cations/anions (groundwater)

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Encapsulation Technology PFASs – The ‘X55’ Product

Containment/Ecapsulation

Crystallization
X55 product applied undergoes crystallization reaction into the base materials matrix utilizing the moisture in which PFASs are retained.

Barrier
This reaction creates a long lasting waterproof barrier containing and encapsulating the PFAS. The X55 product has been proven to be chemically resistant to organic and inorganic contaminants, acids, weathering effects like temperature variations, increases in air pollutants, salt effects, etc.

1. Restricting leaching/movement of the PFAS contaminant into the environment;

2. Controlled-encapsulation and stabilization of PFAS contaminant such that it can potentially be disposed at a less restrictive and less costly disposal facility or reuse on site.

3. Ongoing use of PFAS contaminated source area with regulatory approval, allowing future disposal and mitigation programs that are commercially viable.

ADSORPTION/
SEPARATION

FIXATION

DESTRUCTION

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Sonolysis

Applicability:

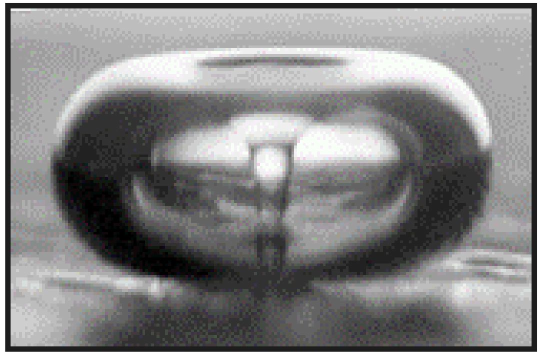
- Ultrasound applied to water results in successive rarefaction/compression of microbubbles ultimately yielding cavitation with extremely high temperatures on the surfaces of the bubbles resulting in pyrolysis of PFAS.

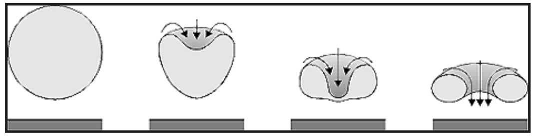
Benefits:

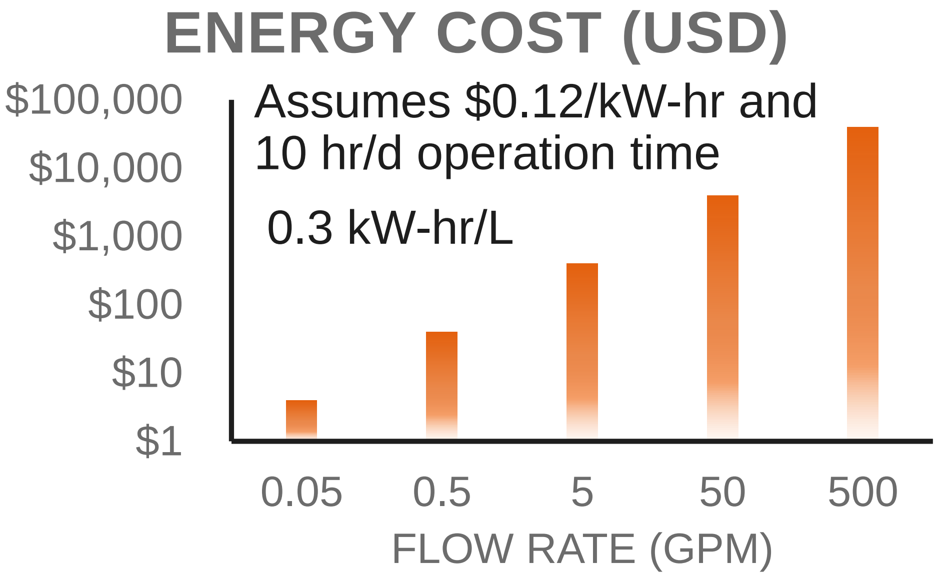
- Can reliably destroy concentrated PFAS waste streams with literature supported fluoride mass balance.
- Opportunities to use green energy sources as technology develops (i.e., solar power).

Limitations:

- PFOA rate > PFOS rate. PFOS will require longer residence times and/or more energy. Effective below 10,000 ppt?
- Requires specialized equipment and skilled implementation.
- High energy consumption and low flow rates.







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Electrochemical Degradation

Applicability:

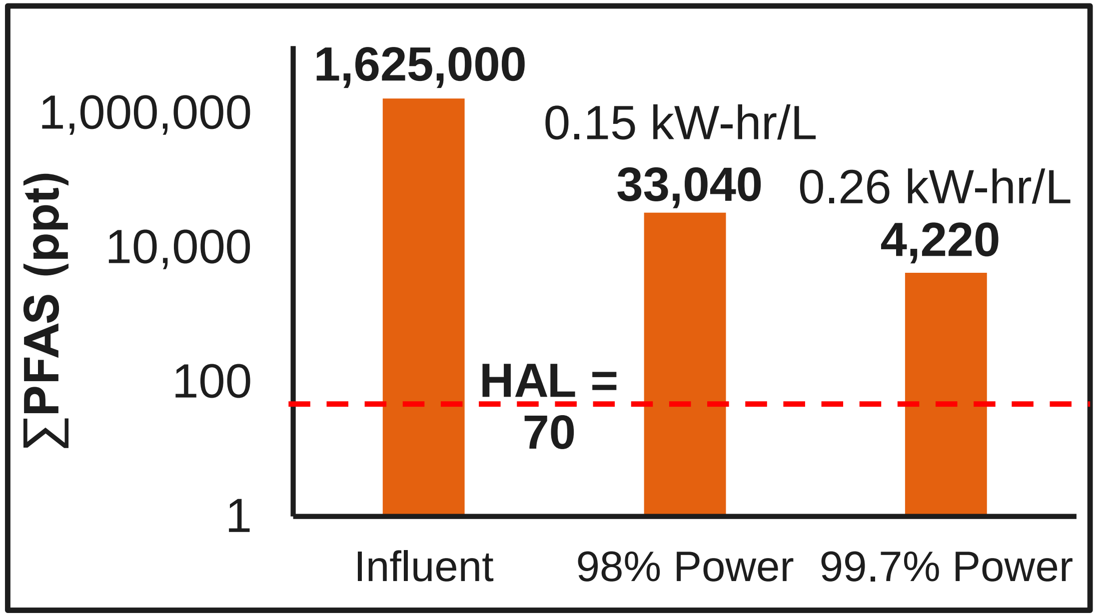
- Electrochemical cells can degrade PFAS through direct electron transfer at the surface of the anode.

Benefits:

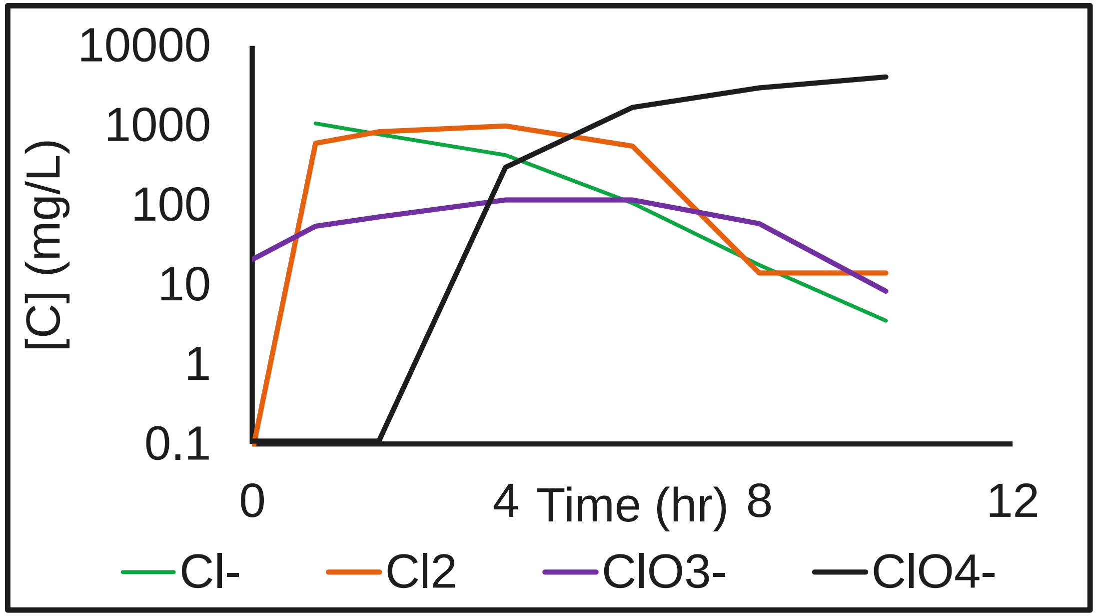
- Provides a feasible destruction mechanism for concentrated PFAS waste streams at low flow rate.
- PFAS degradation confirmed (fluorine mass balance); effective for both laboratory and real groundwater/wastewater.
- Less energy consumption than sonolysis.

Limitations:

- Geochemical constituents may cause secondary concerns (i.e., chloride oxidized to perchlorate).
- Acidity around anode may facilitate PFOS sorption; needs further investigation. Confirmed effectiveness for sulfonates?
- Short chain PFAAs appear to be recalcitrant at low current density (<50 mA/cm^2).
- Lowest demonstrate concentration >1,000 ppt



Gomez-Ruiz et al 2017



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Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors

Zhanyun Wang [a], Ian T. Cousins [b], Martin Scheringer [a,*], Konrad Hungerbühler [a]

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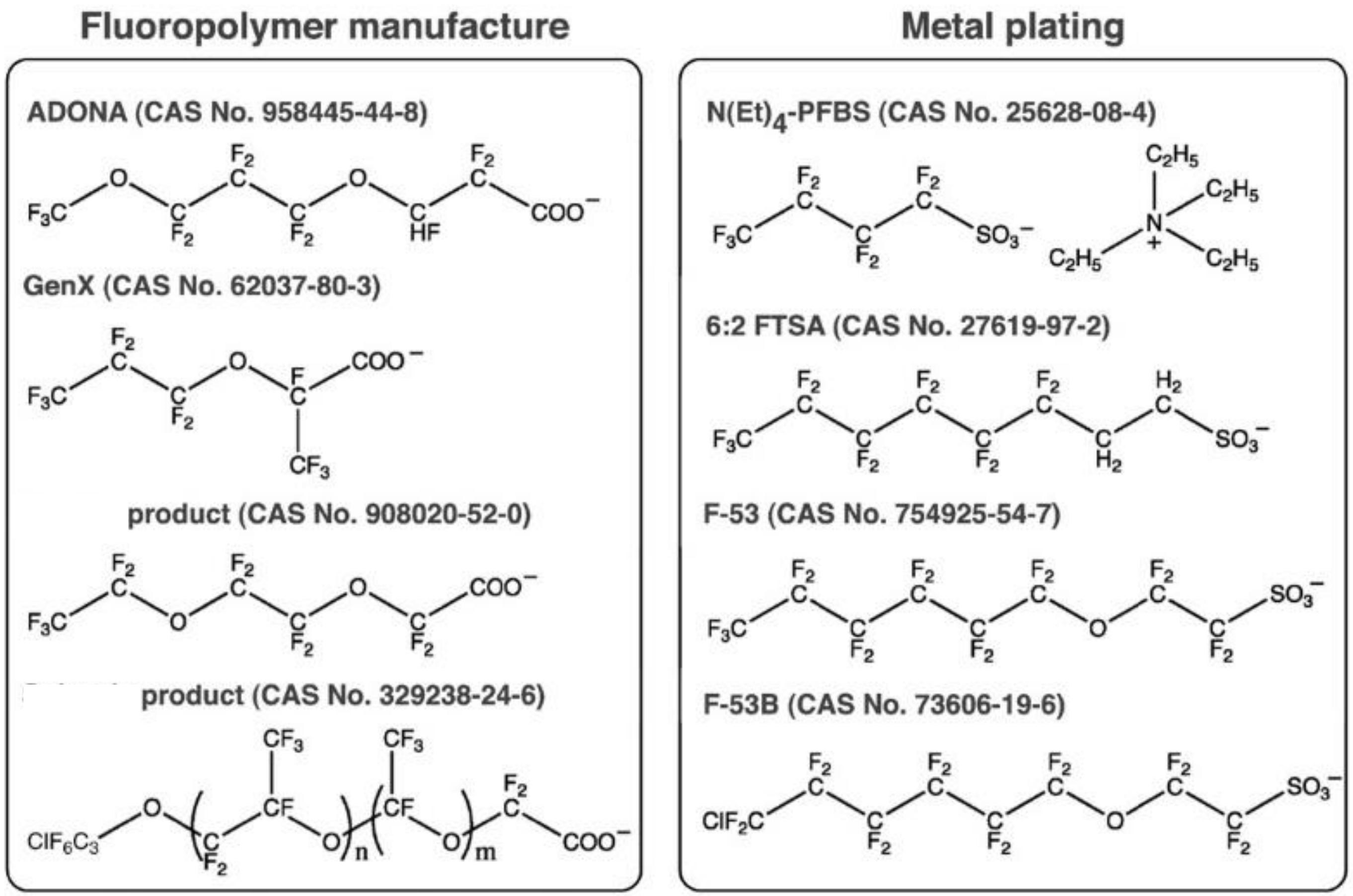

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Summary

- Recalcitrant PFAS chemistry and precursor loading are relevant in remediation consideration
- *Ex situ* treatment trains are the current state of the practice for groundwater
- Few practical destructive techniques exist, with some in development
- “Quick fix” interim remedial actions come with a life-cycle price tag
- Don’t abandon institutional knowledge (myth busting, Remediation Hydraulics principles, etc.)!

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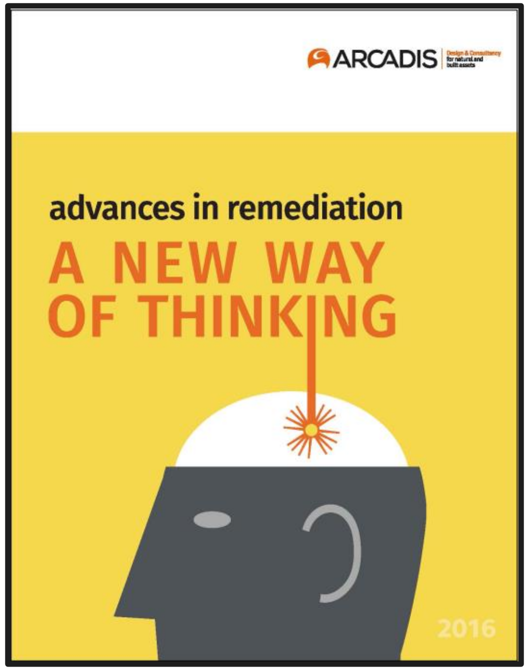
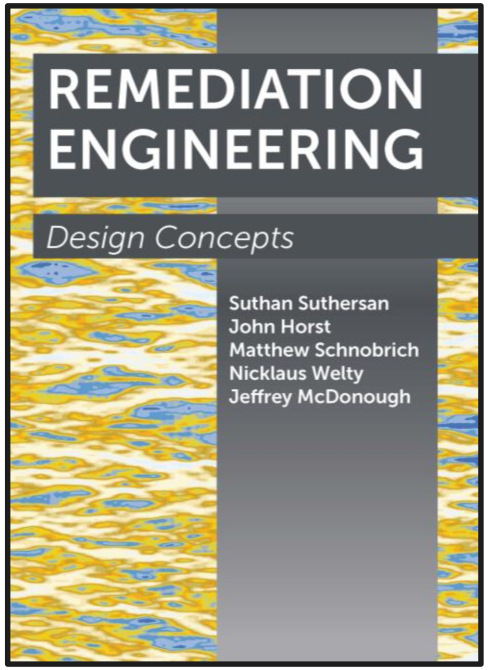
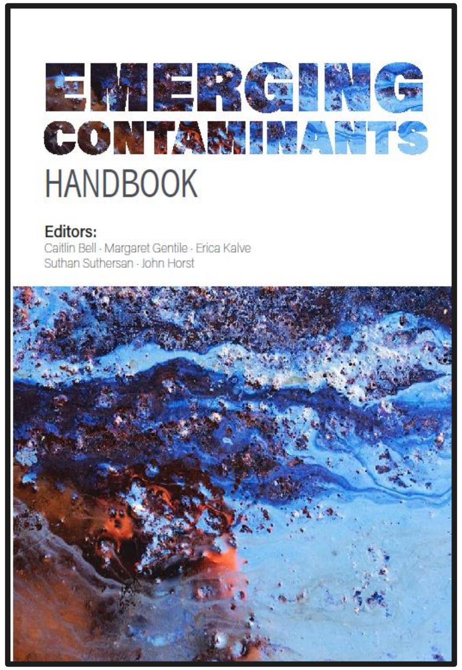
Ask Us About These New Resources!







Download at:
https://www.concawe.eu/publications/558/40/Environmental-fate-and-effects-of-poly-and-perfluoroalkyl-substances-PFAS-report-no-8-16

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