In-Site Immobilization and Beyond: Leveraging Biochar and Phytoremediation for Successful Site Management of PFAS

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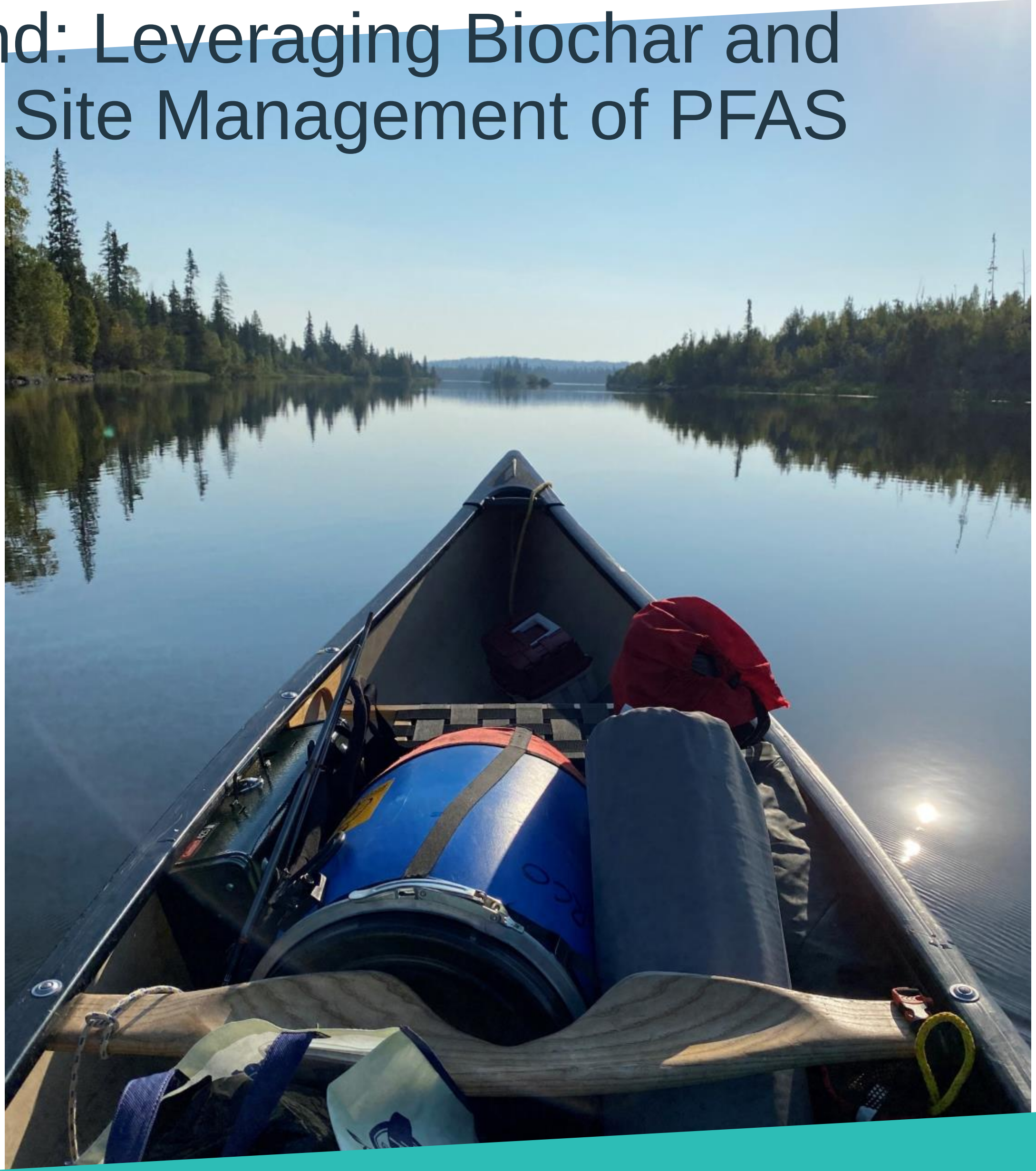
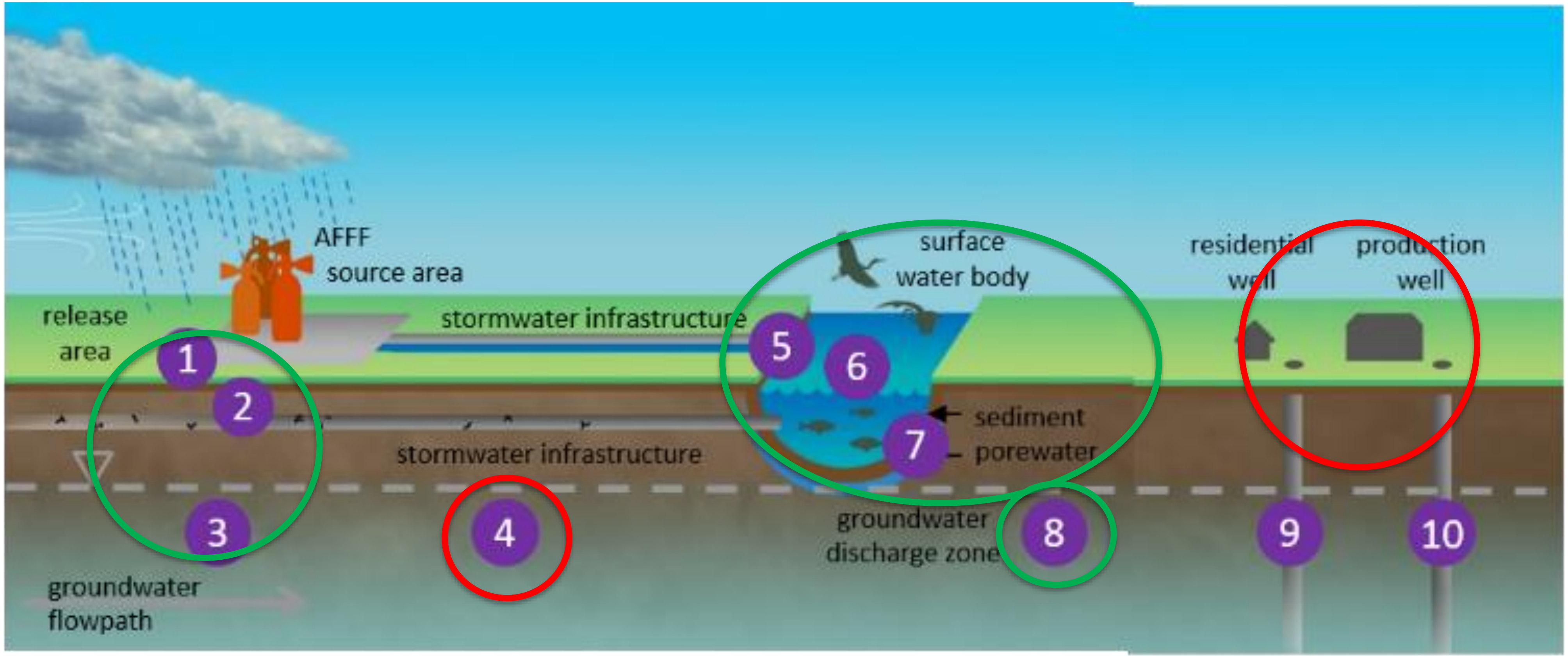


CSM and Remediation Scenarios



1. Surface soil
2. Subsurface soil
3. Source area GW
4. Downgradient GW containment
5. Stormwater infrastructure containment
6. Surface water
7. Sediment
8. Offsite GW impacted by surface water
9. Residential well GW treatment
10. Production well GW treatment

Focus Thus Far

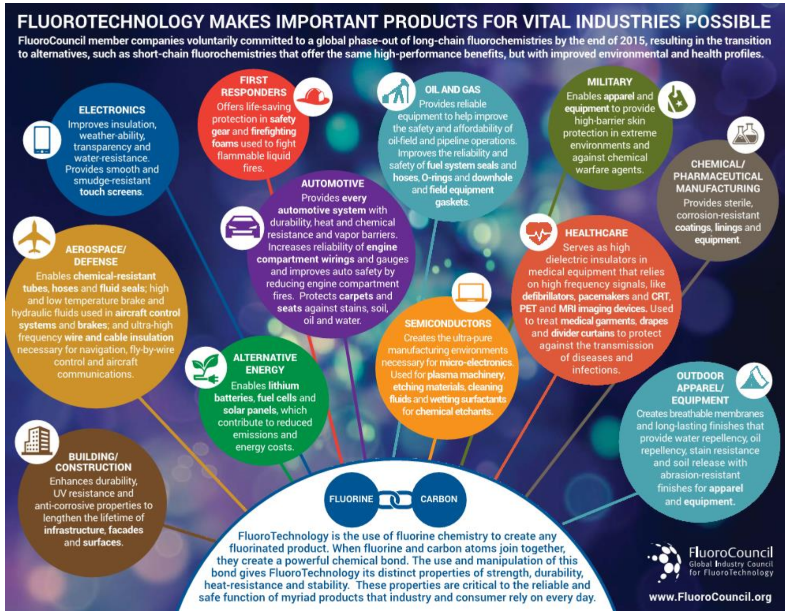
Targeted Future Focus

PFAS treatment via application of biochar in existing infrastructure, engineered systems, soil and groundwater

Benchtop Studies

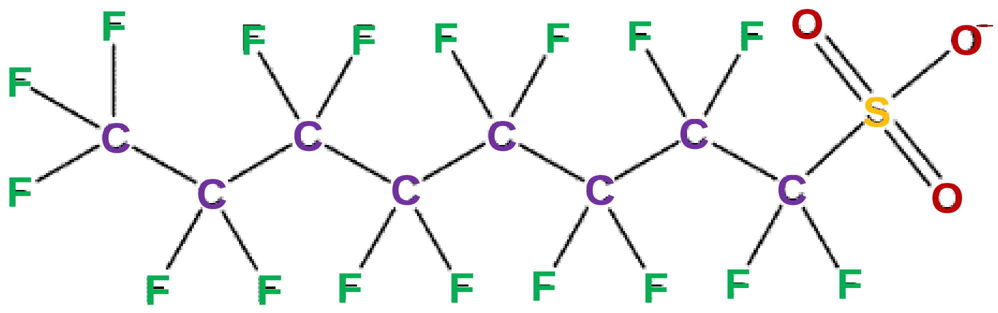
PFAS – Emerging Contaminants of Concern

- Family of widely used compounds
- ***Strong carbon-fluorine bond***
- Persistent in environment "Forever Chemicals"
- Surfactants with hydrophobic "tails" and hydrophilic "heads"
- Cationic (+), anionic (-), or zwitterionic (+ and -)



Hydrophobic Tail (Affinity: Air, NAPL, Carbon etc)

Hydrophilic Head (Affinity: Water)



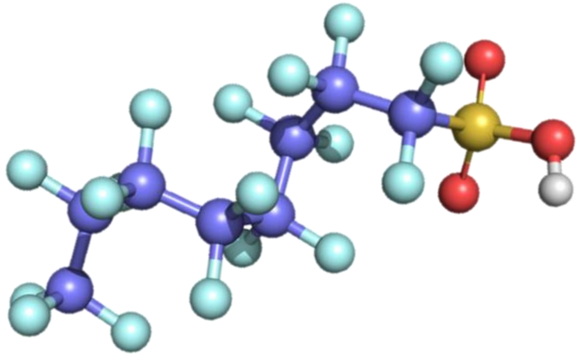
PFOS - perfluorooctanesulfonic acid

Outline

- Per and polyfluorinated alkyl substances (PFAS)
  - Why carbon?
- Biochar applications

  Benchtop 1.0

  Field Results



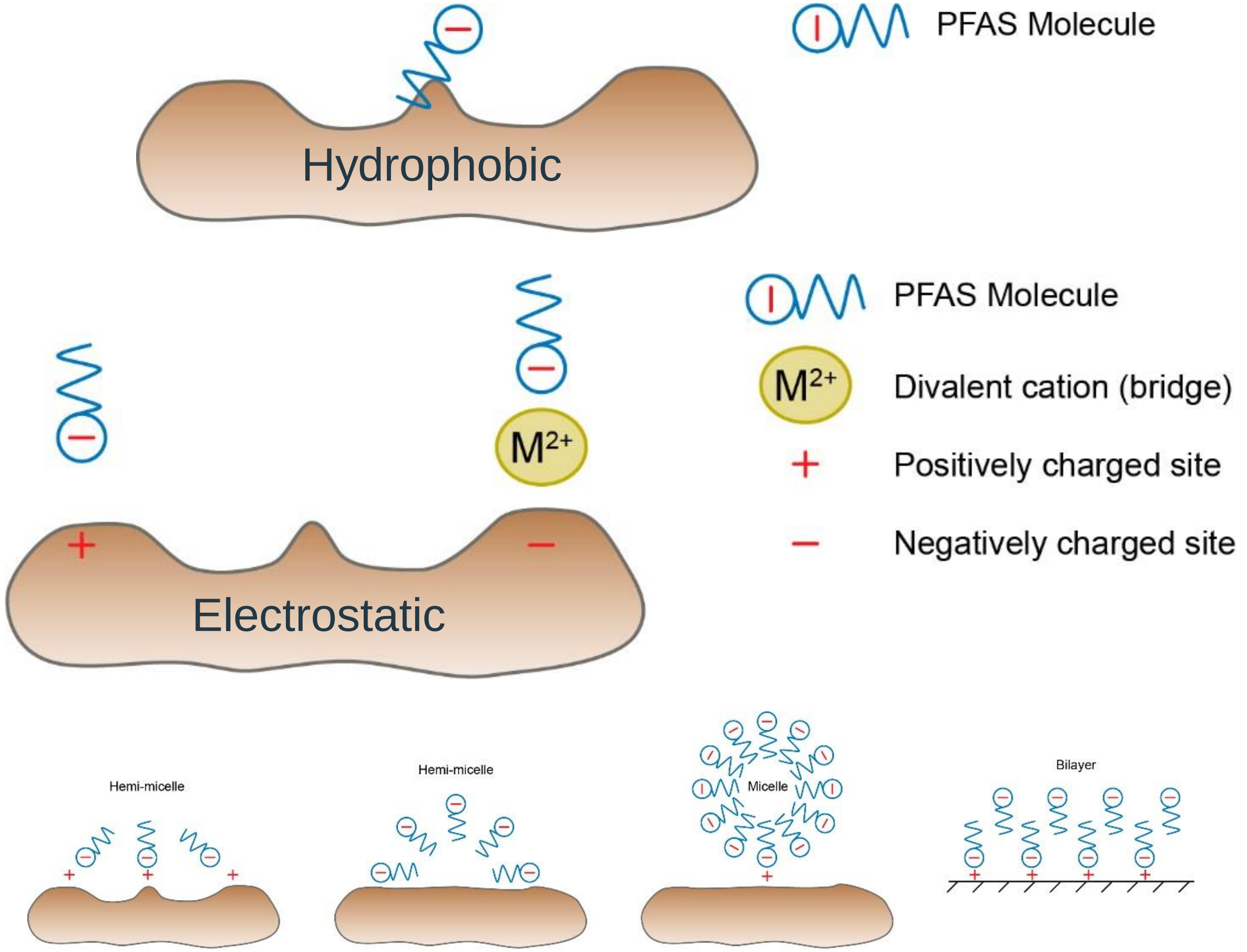
Why Carbon?

In-situ tools are limited.

Head and Tail factors that influence PFAS sorption onto carbon

- Hydrophobic attraction
- Electrostatic attractions? Carbon and clays typ. have local charge
- Divalent cations may provide “bridge” for electrostatic binding of PFAAs (negatively charged sites)
- Micelle/hemi-micelle sorption?

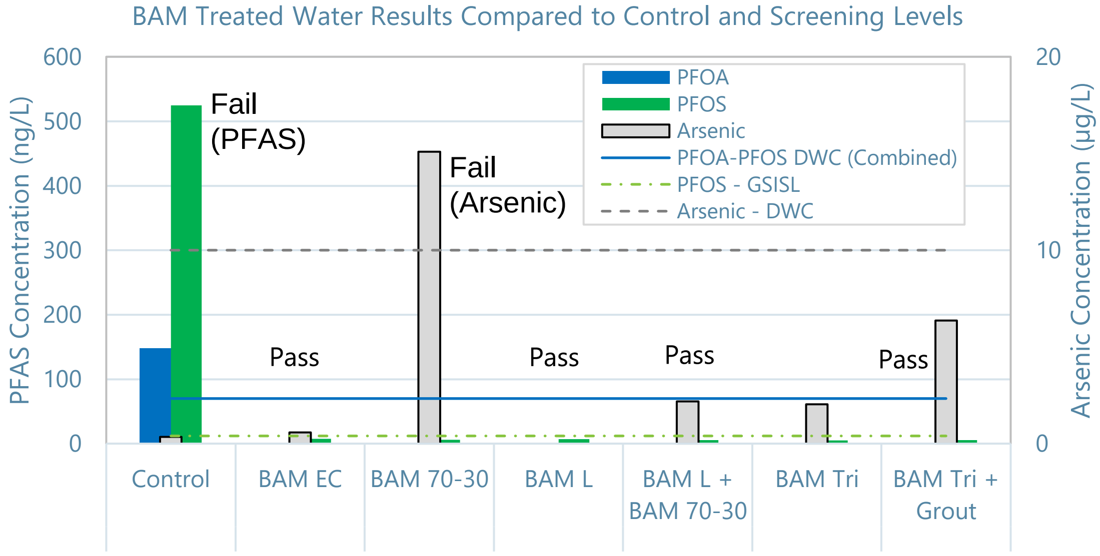
Carbon enhancements may retard migration by more than one mechanism.

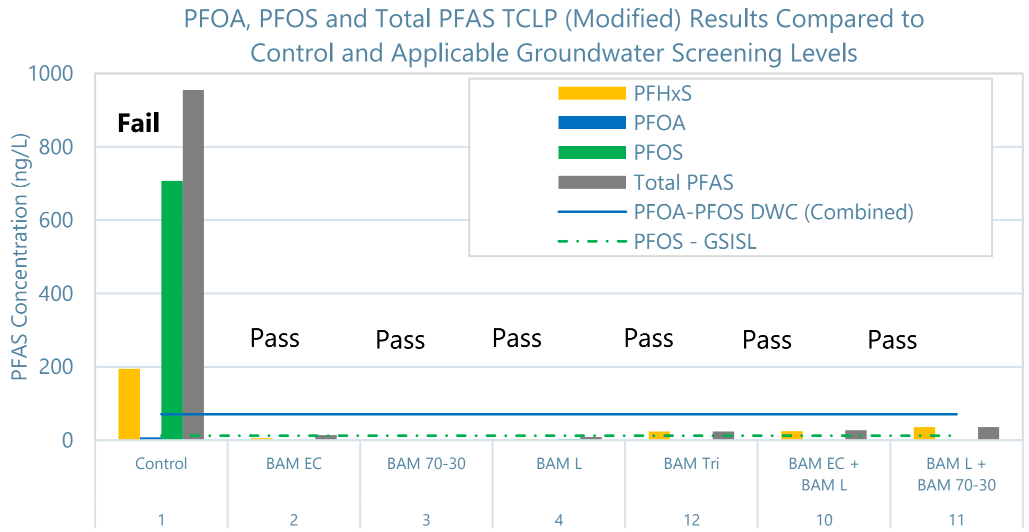


Potential Interactions
Modified from Z. Du et al 2014

PFAS – Immobilization Study - Benchtop

- Dec 2017 Benchtop Study
- ORIN Technologies (ORIN) treated Site soil and groundwater at loading rates of 3% to 5% with:
  - Bioavailable Absorbant Media (BAM^{TM})
  - BAM^{TM} and organoclay/bentonite mixture
  - BAM^{TM} with Fenton's Reagent (simulated oxidation – worst case/precursors)
- BAM^{TM} effectively treated groundwater
- BAM^{TM} reduced TCLP (metals)





PFAS treatment via application of biochar in existing infrastructure, engineered systems, soil and groundwater

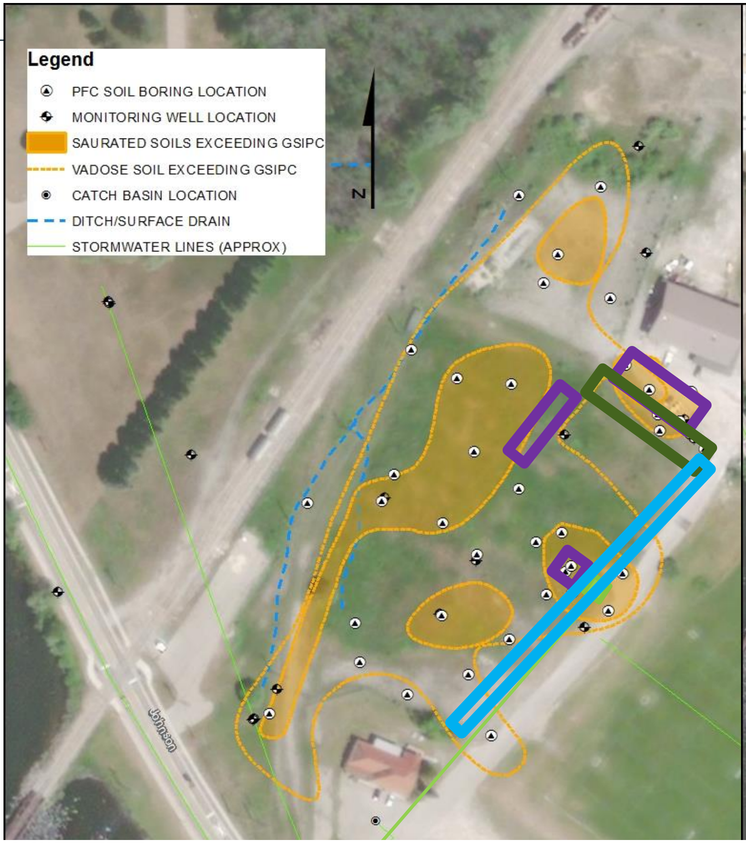
Experimental Site

Site Context – PFAS in Soil & Groundwater – Biochar Applications

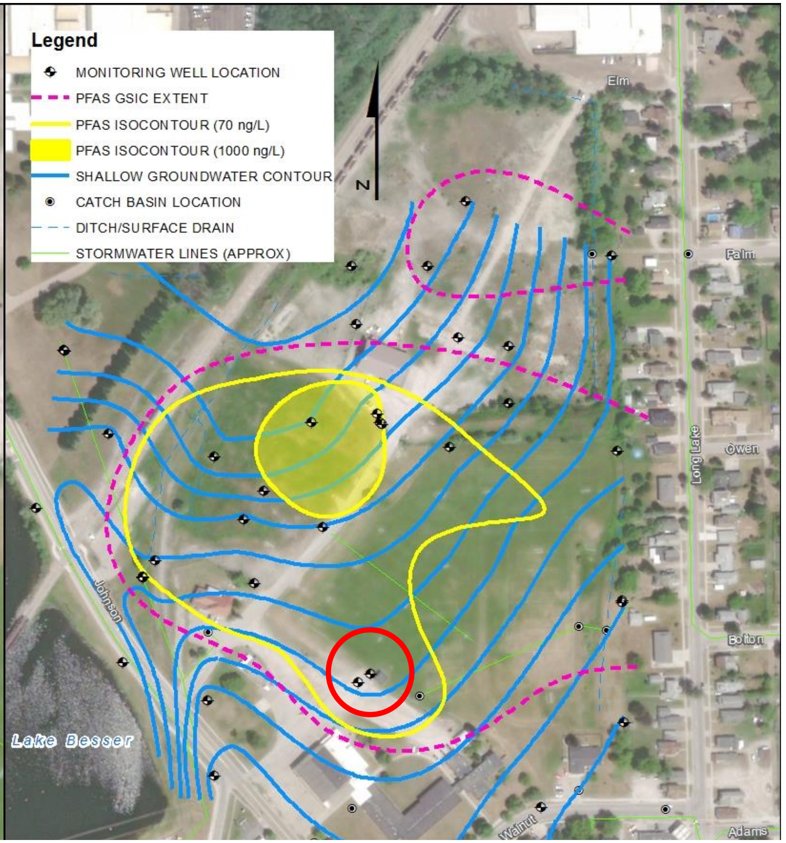
- Can biochar:
  - Reduce leaching from the “smear zone”?
  - Contain PFAS in the source?
  - Mitigate PFAS migration into/via storm water?
  - Act as an effective PRB?

PFAS	Soil		Groundwater	
	ng/g (ppb)	*f* (%)	ng/L (ppt)	*f* (%)
PFBA	ND	0%	493	92%
PFBS	5.7	11%	*3,140*	85%
PFHxS	43	56%	*15,400*	79%
PFOS	264	63%	**9,190**	74%
PFOA	5.4	9%	**804**	79%
Total (537)	14 – 76% samples		20 – 92% samples	

Italics – exceeds drinking water standard
Bold – exceeds drinking water & surface water standards

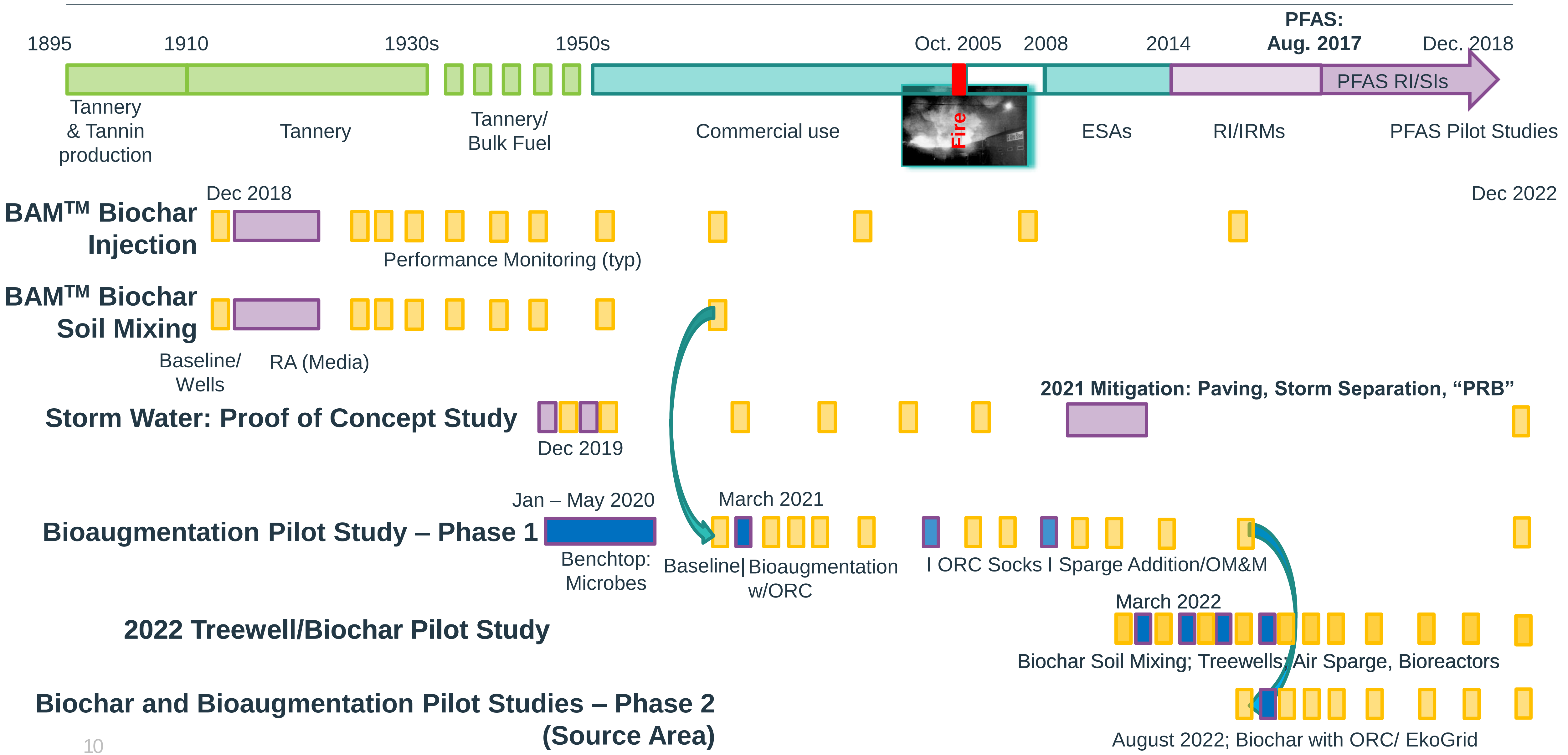


- Widespread <0.5mbgs (High Water)
- Hotspots 1.5 mbgs (Low Water):
  - Former building footprint
  - Topographic lows/infiltration areas
- Limited detections at base of aquifer



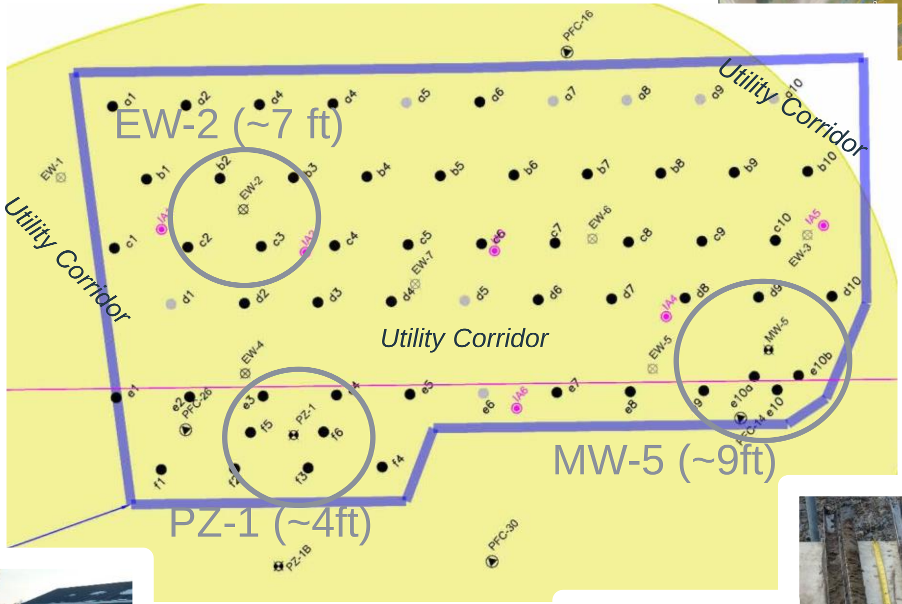
- Expanding plume
  - In contact with onsite storm water infrastructure (Thunder Bay River)
  - Migrating towards Lake Huron
- PFOA Hot Spot - downgradient
- Offsite fractionation: PFBA+PFBS, followed by PFOA then PFOS

Biochar-Related Corrective Action Pilot Studies



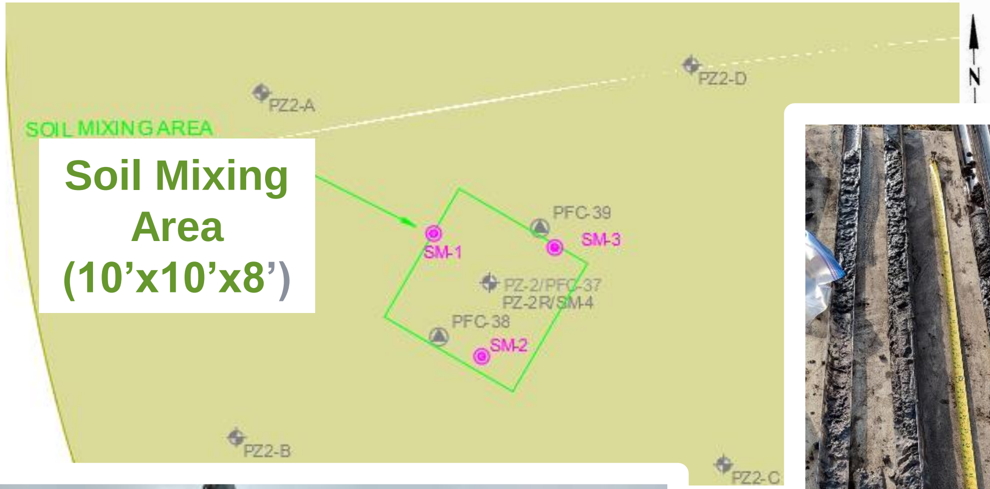
December 2018 Biochar Injection Pilot Test

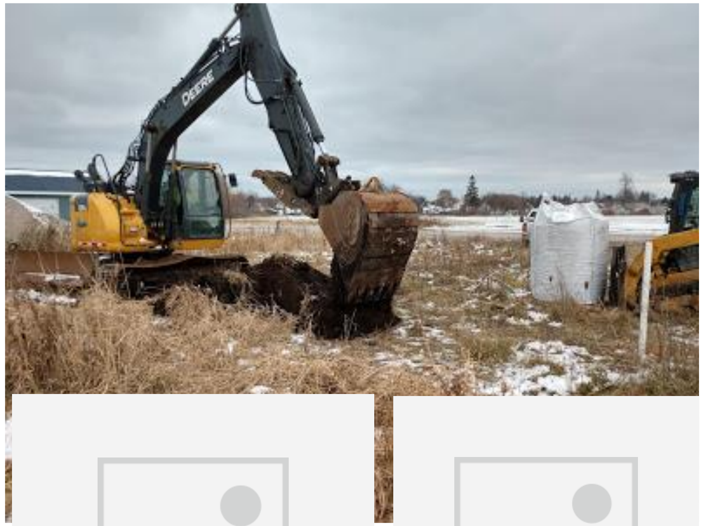
- 30 µm BAM-Ultra™ - solid media mixed into slurry in treatment trailer
- 46 Injection locations (typ 2m centers) ~10m x 25m)
- Bottom up Injection (0.5m lifts, 0.5 - 3m bgs)
- Treatment vol: 10m x 25m x 2.5m ~ 650m^3
- 100 gallons of 12.4% BAM-Ultra™ solution injected at each location (2,400 kg)
- **Push -** Injection pressures of 40 – 100 psi
- **Pull -** Vac Truck, 7 extractions wells + existing wells. 32 m^3 of liquid waste (Treated in frac tank with BAM-X™)



December 2018 - Soil Mixing Pilot Test

- Location – Future storage unit buildout
- Excavator, skid steer & 2m^3 Super Sack of BAM-X^{TM}
- 725 kg of BAM-X^{TM} Mixed into 23m^3 (~1.5% loading dry weight or ~6.75% by volume)
- Soil and BAM mixed in place – through the "smear zone"
- Post mixing cores: ~homogeneous





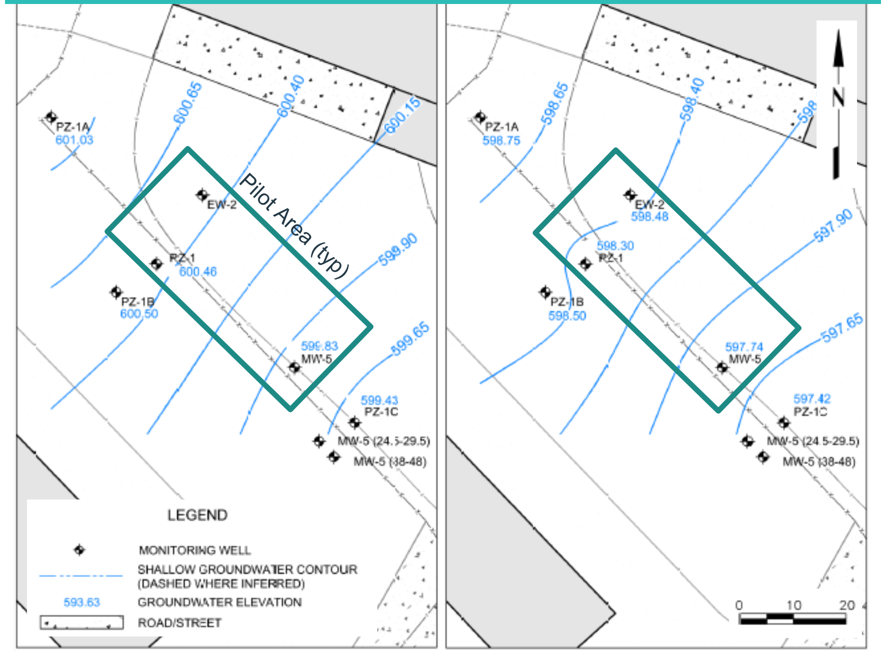
Hydraulic Results

- Hydraulic Conductivity decreased where more permeable sands present (PZ-1)
- Hydraulic conductivity increased in tighter soils requiring higher injection pressure (i.e. fractures; MW-5)

Location	Test	Pre-Pilot K	Post Pilot K
MW-5	Injection	$1x10^{-5}$	$3x10^{-5}$
PZ-1	Injection	$6x10^{-5}$	$3x10^{-5}$
PZ-2/2R	Soil Mixing	$4x10^{-5}$	$3x10^{-6}$

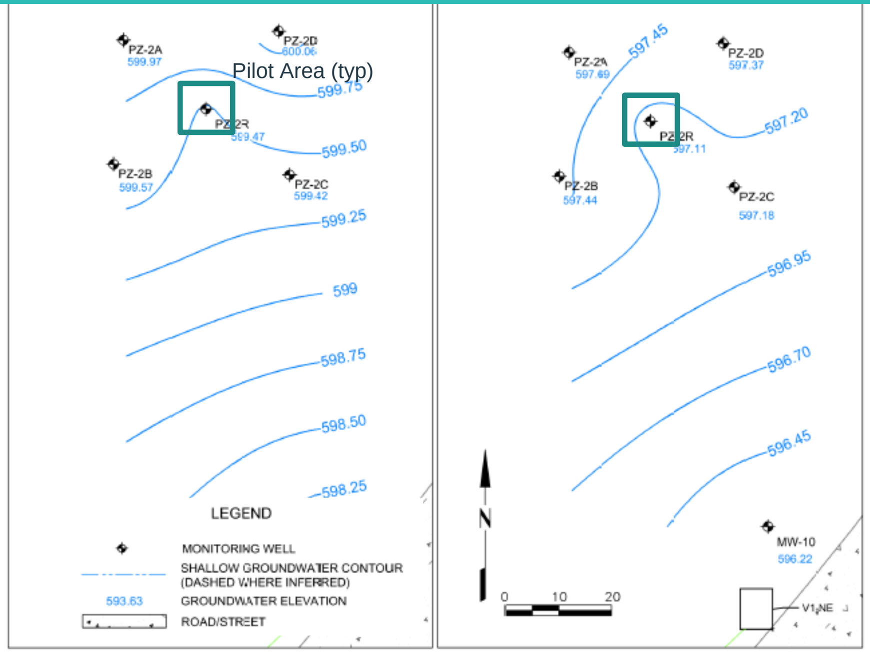
K = Hydraulic conductivity in m/sec

Groundwater Contours – Injection Area



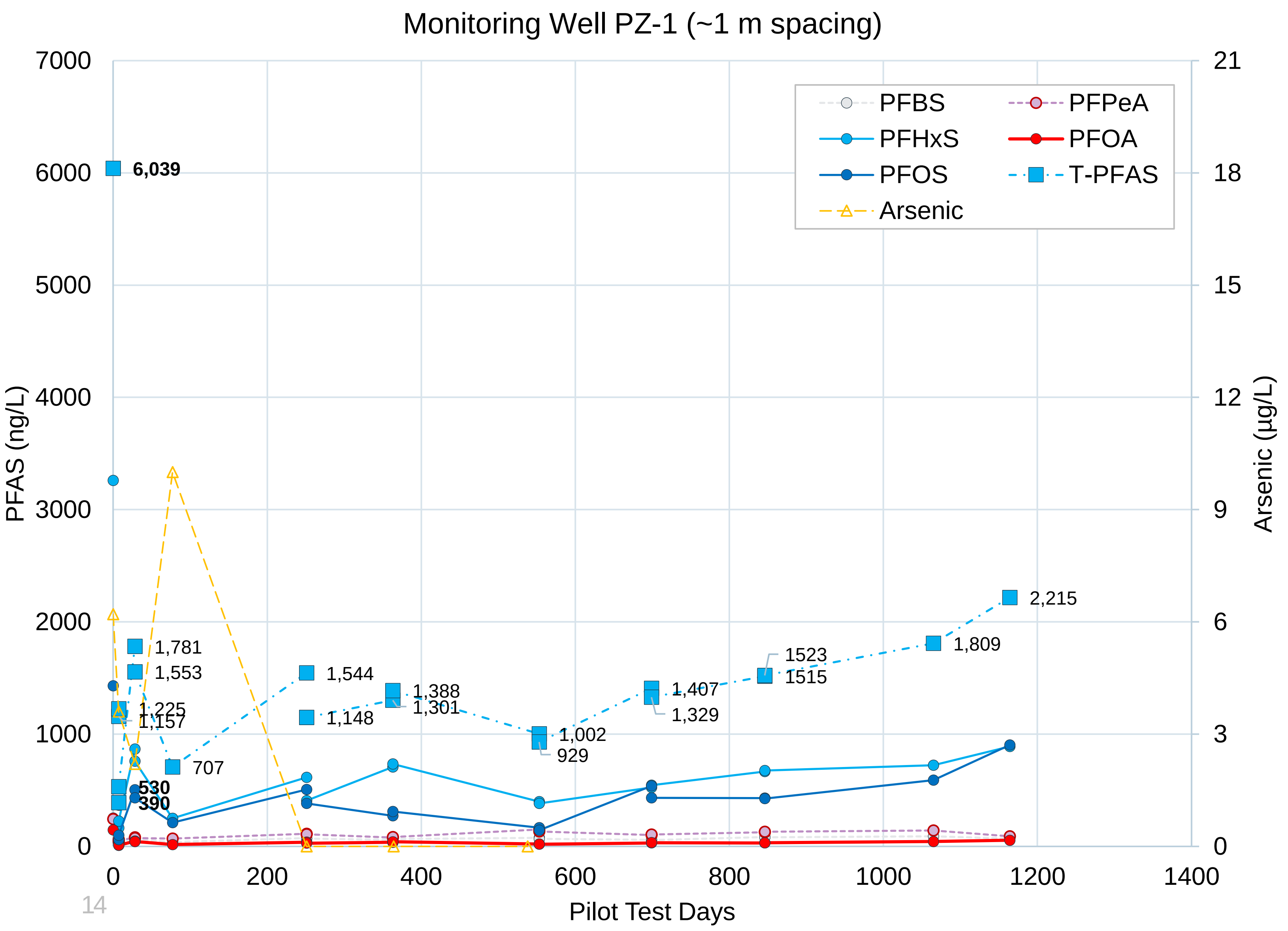
FALL 2018 SUMMER 2019

Groundwater Contours – Soil Mixing Area



FALL 2018 SUMMER 2019

Groundwater Injection Results – 1 m array (~1% Loading Rate)

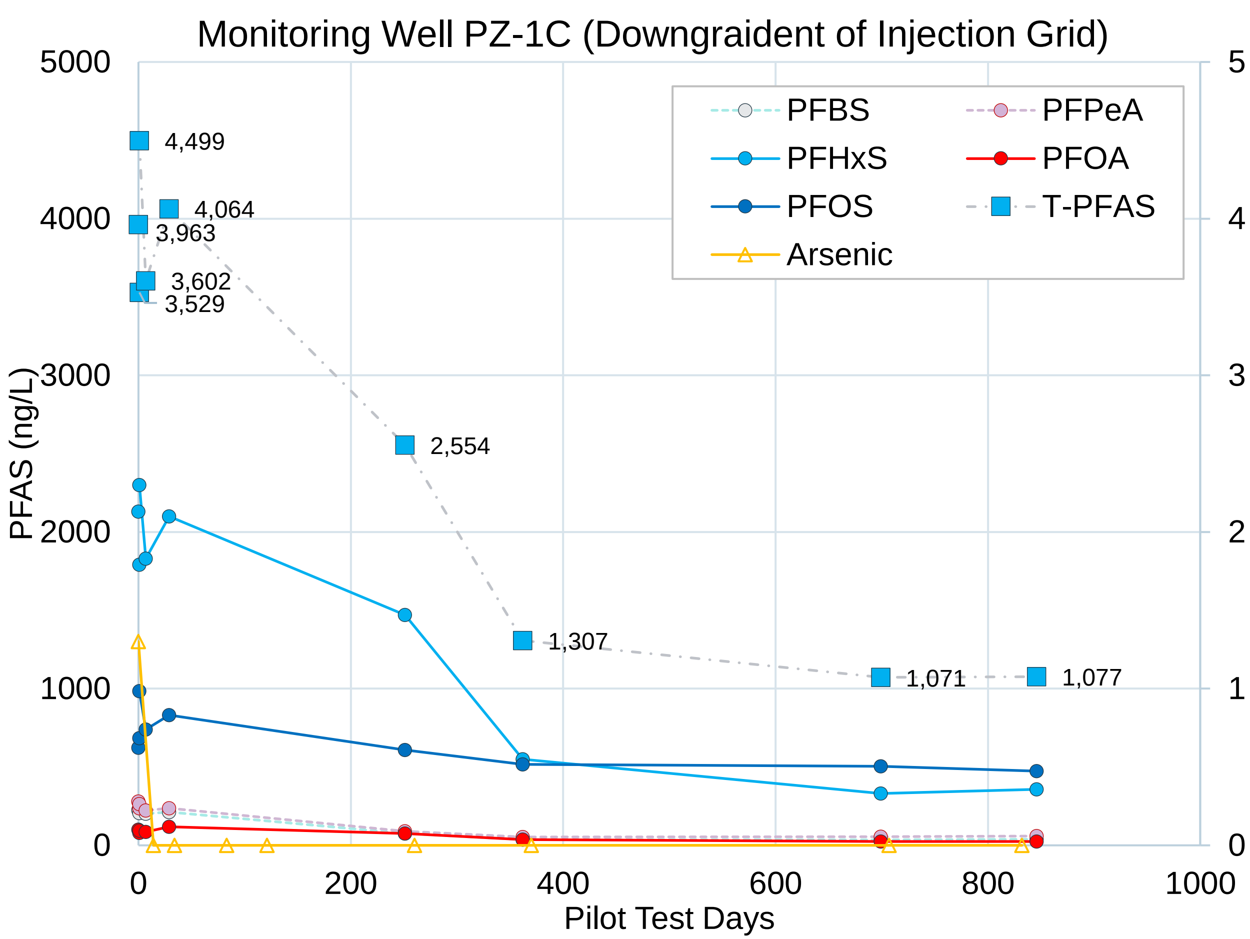


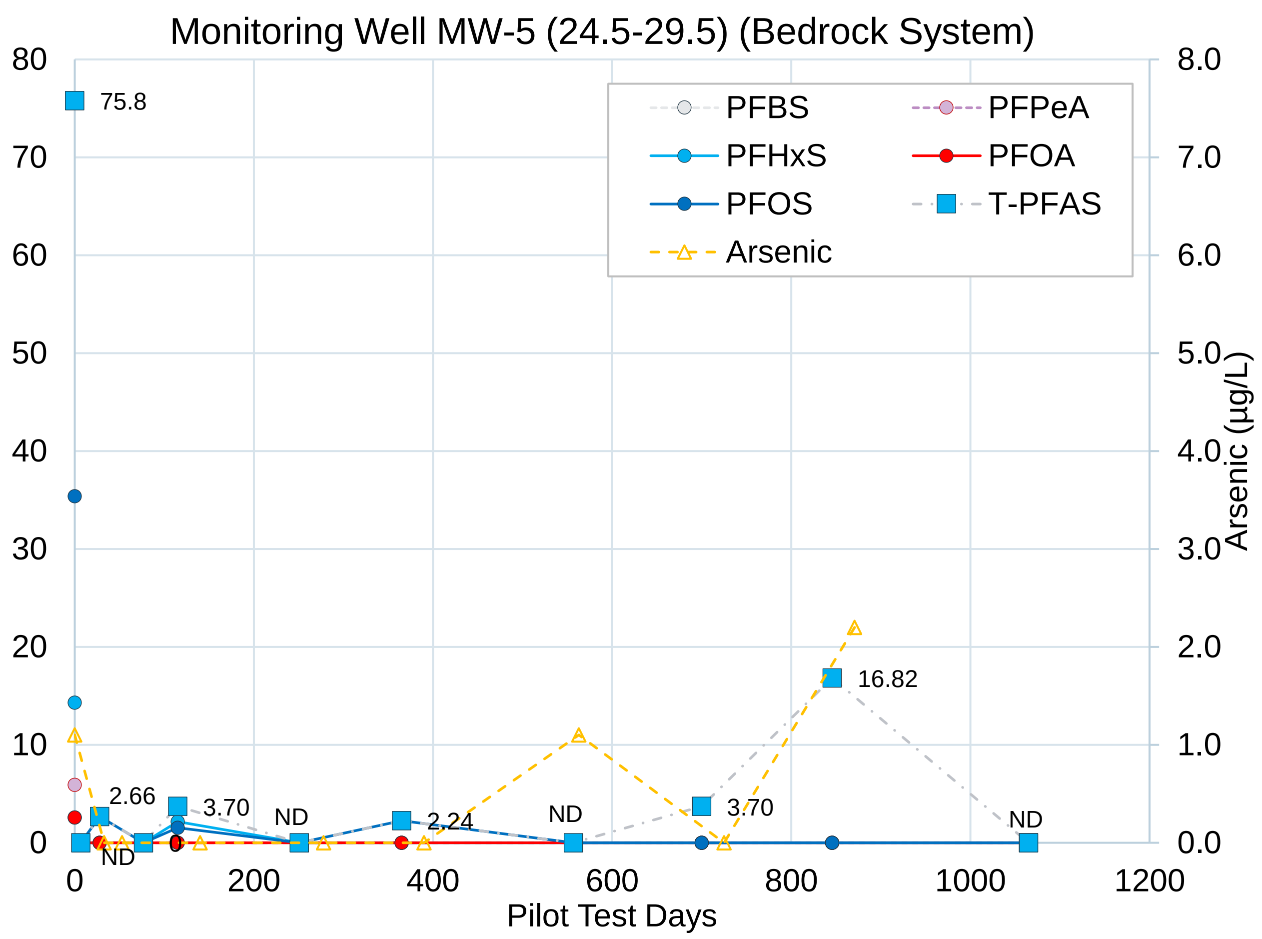
PFAS		Percent Reduction
PFCA	PFBA	60 (68)
	PFPeA	63 (84)
	PFHxA	73 (89)
	PFOA	63 (95)
PFSA	PFBS	73 (89)
	PFHxS	73 (95)
	PFOS	37 (96)
	8:2FTS	100 (100)
T-PFAS		63 (94)

(Maximum percent reduction observed)

- Maximum reductions in first week
- Short chain/long chain reductions even out over time
- PFOS percent recoveries declined at year 3.2; Flux, leaching or transformation?

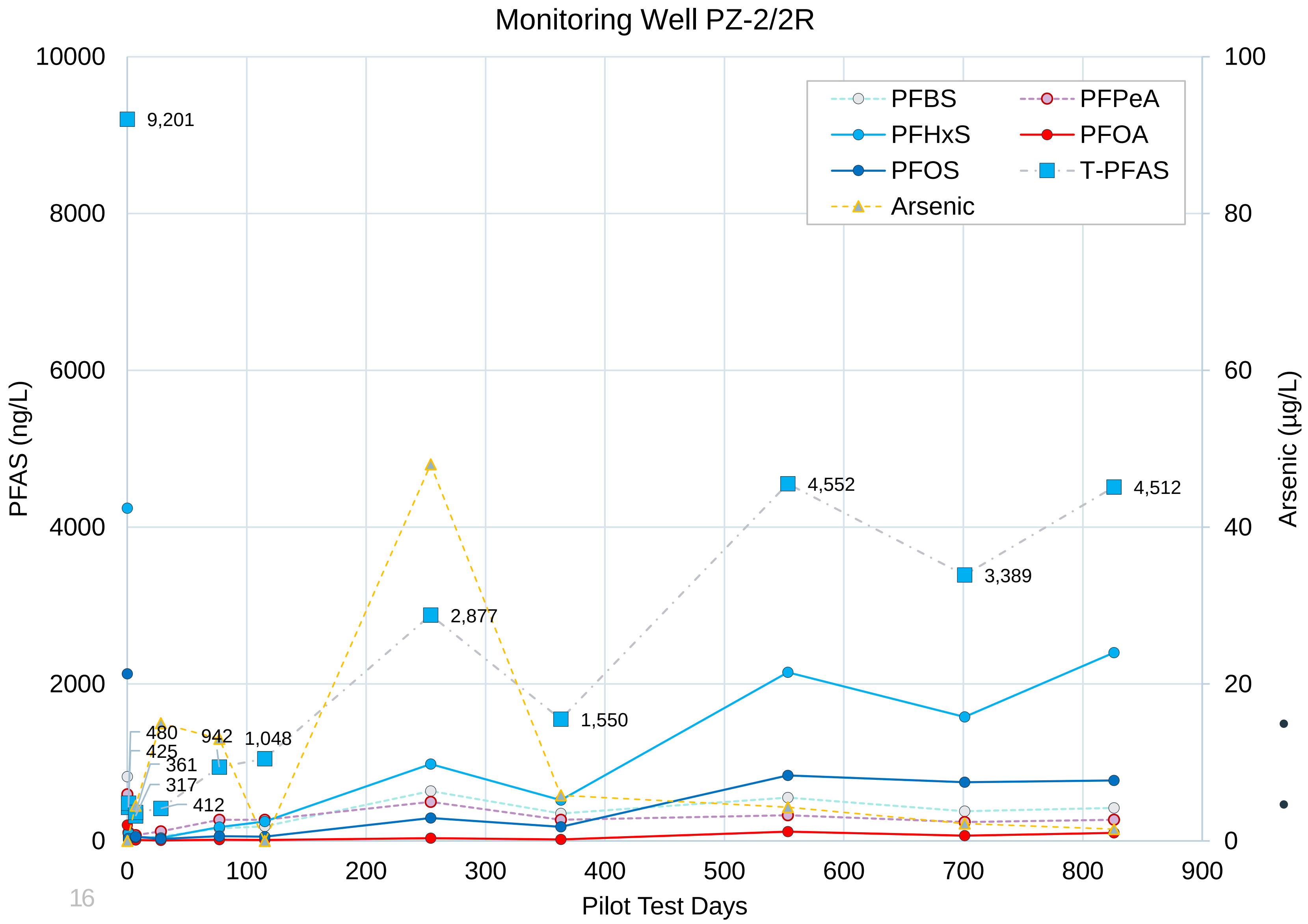
Groundwater Injection Results – Downgradient and Below Treatment Area





- 76% Reduction in total PFAS flux downgradient at PZ-1C (PFPeA >90%); no Arsenic bump
- Flux reduced to bedrock quickly and sustained; minor upticks during spring (high water table)

Groundwater Results – Soil Mixing Area



PFAS		Percent Reduction
PFCA	PFBA	44 (59)
	PFPeA	55 (88)
	PFHxA	53 (96)
	PFOA	52 (98)
PFSA	PFBS	49 (97)
	PFHxS	43 (99)
	PFOS	64 (99)
	8:2FTS	ND
T-PFAS		51 (97)

(Maximum percent reduction observed)

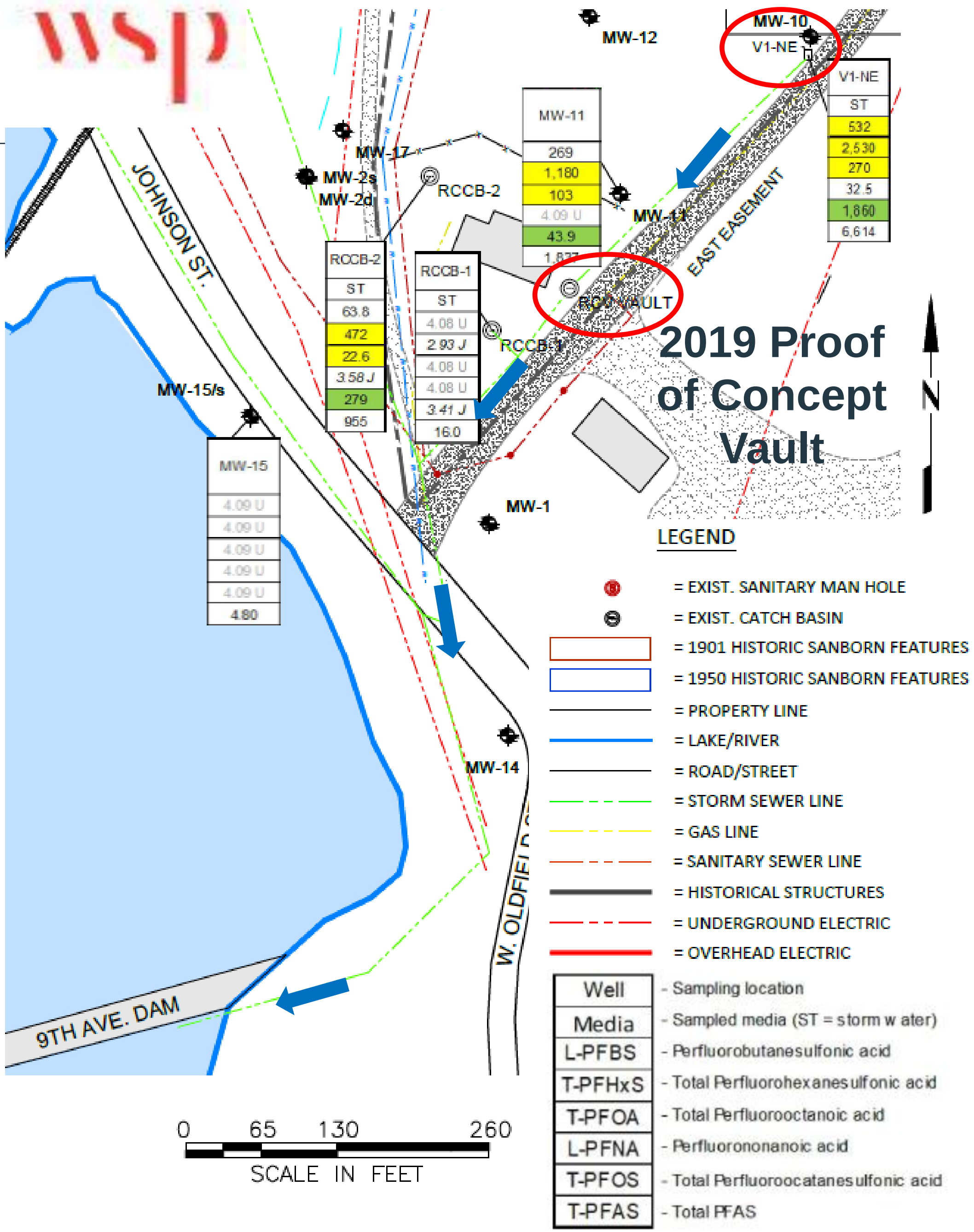
- Maximum reductions ~ immediate and signficant
- PFOS percent reductions declined at 2.25 years; Flux, leaching and/or transformation?

PFAS treatment via application of biochar in existing infrastructure, engineered systems, soil and groundwater

Stormwater Mitigation

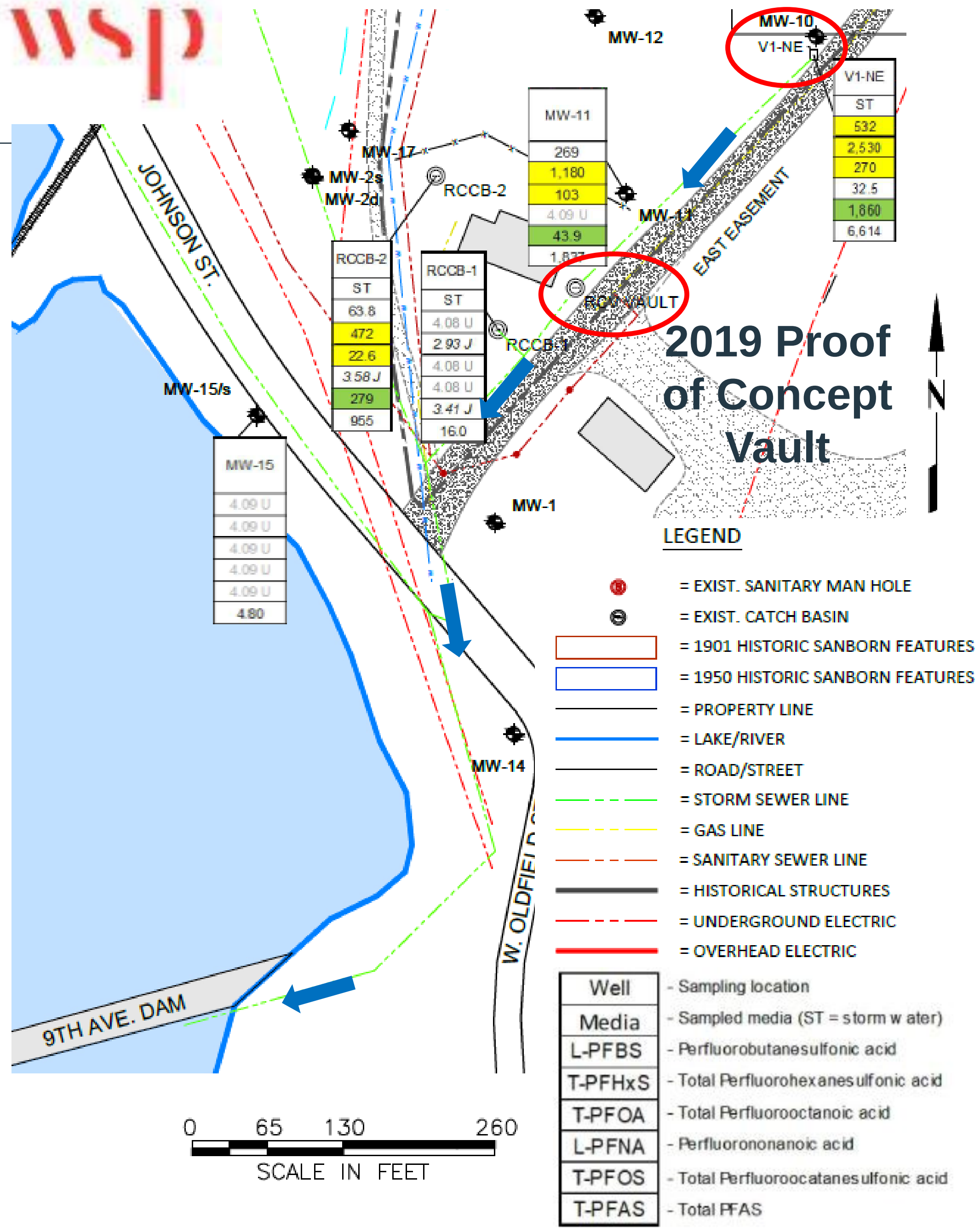
Addressing Storm Water

- Historic tannery storm water system, where intact, remains connected to municipal storm
- Old system in poor shape but continues to manage storm water AND high groundwater (V1-NE)
- Discharge is to Thunder Bay River
- PFOS in storm water as high as 1860 ng/L

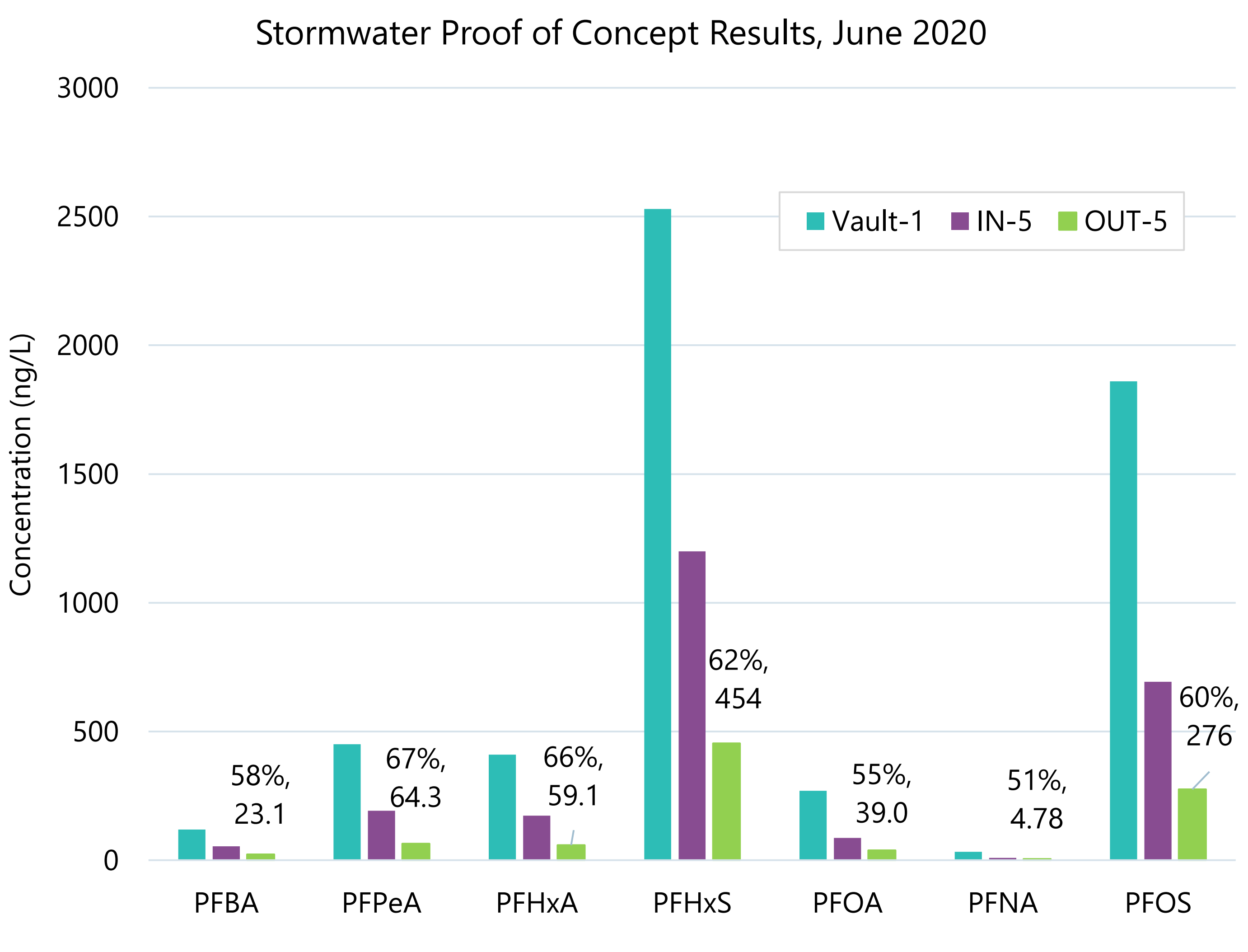


Addressing Storm Water

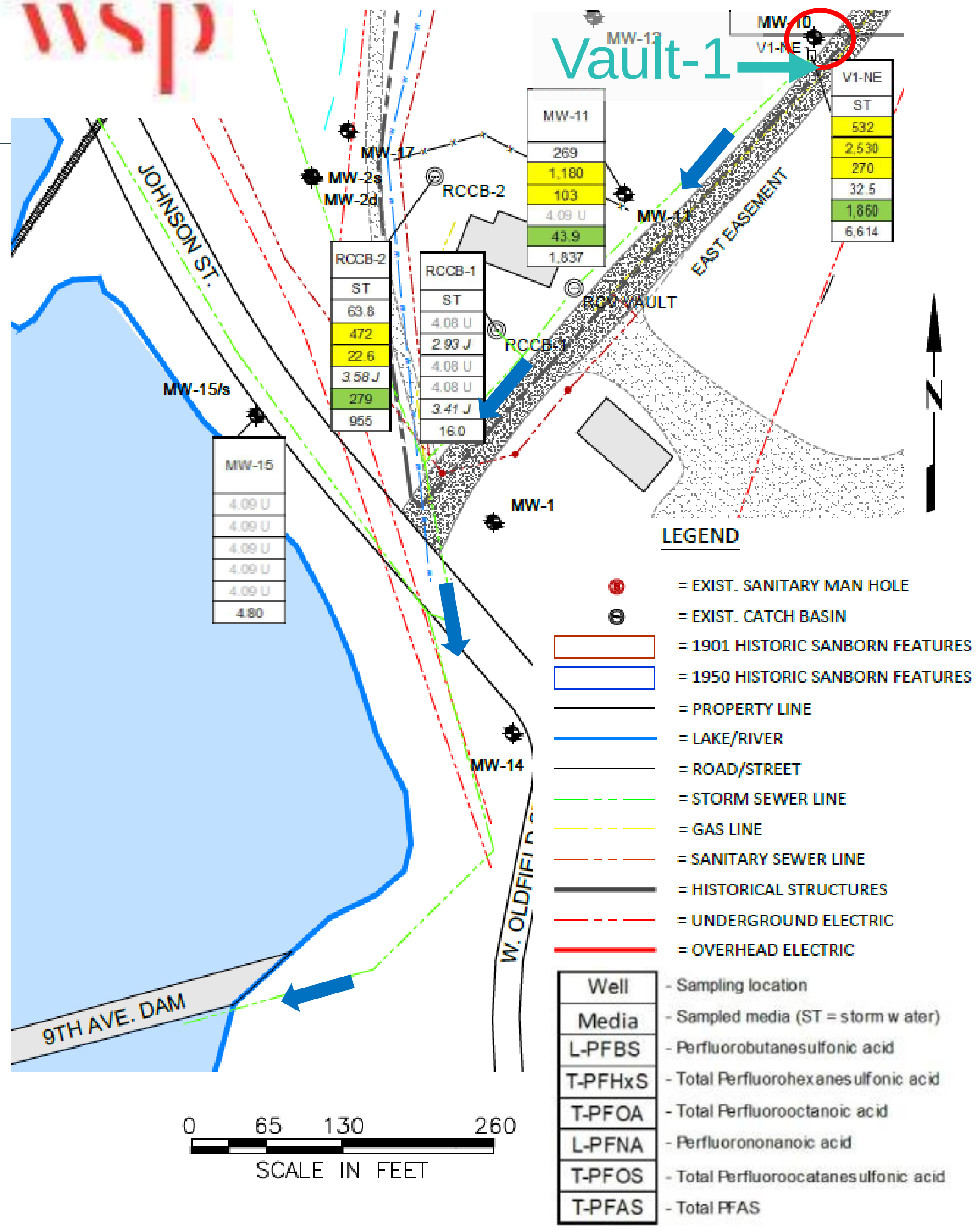
- Dec 2019 Installed BAM™ Booms in existing RCB Vault
- Installed piezometer and four passive sampler collection tubes (IN and OUT)
- Augmented BAM™ in February 2020



Addressing Storm Water

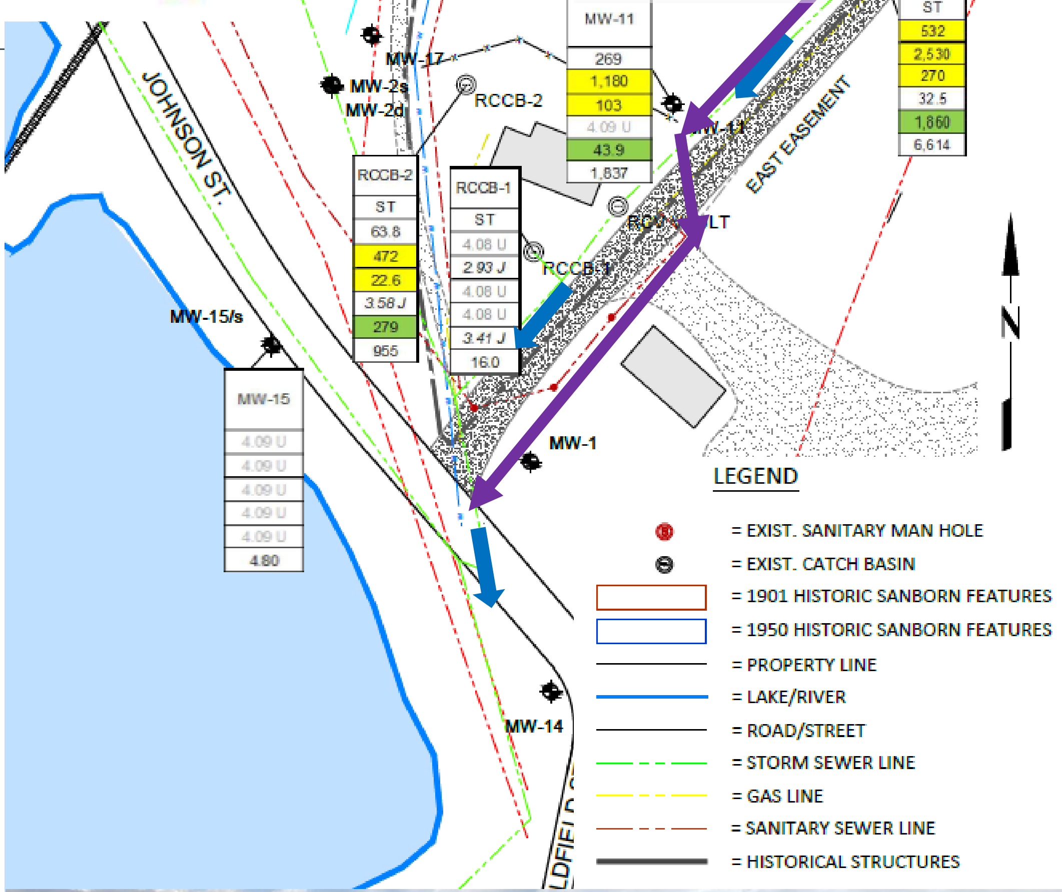


Percent reduction shown based on comparison of the OUT-5 result to the IN-5 result.



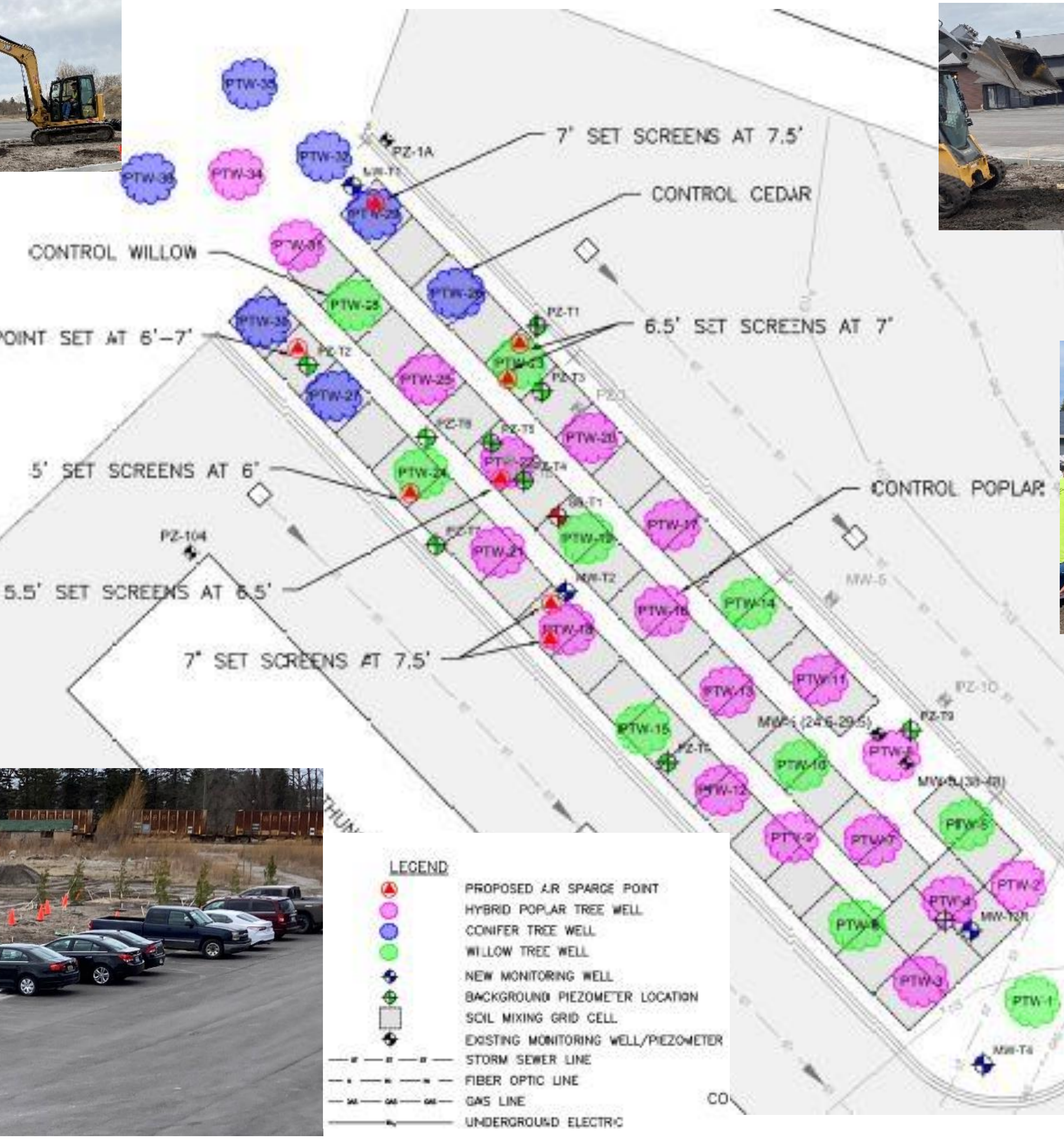
Additional Mitigation – Storm Water Infrastructure

- 2021 – Installed pavement & storm water infrastructure to:
  - Decrease leaching of PFAS from vadose zone
  - Capture precipitation & reduce local, seasonal flooding
  - Isolate conveyance system from groundwater
- What was done:
  - Paved portions of storage units & brewery
  - Installed sealed storm water conveyance infrastructure (bypassing tannery infrastructure)
  - Added BAM to backfill to reduce potential infiltration and immobilize PFAS in groundwater in contact with trench (“PRB”)
  - Performance monitoring wells added in 2022 (*results pending*)



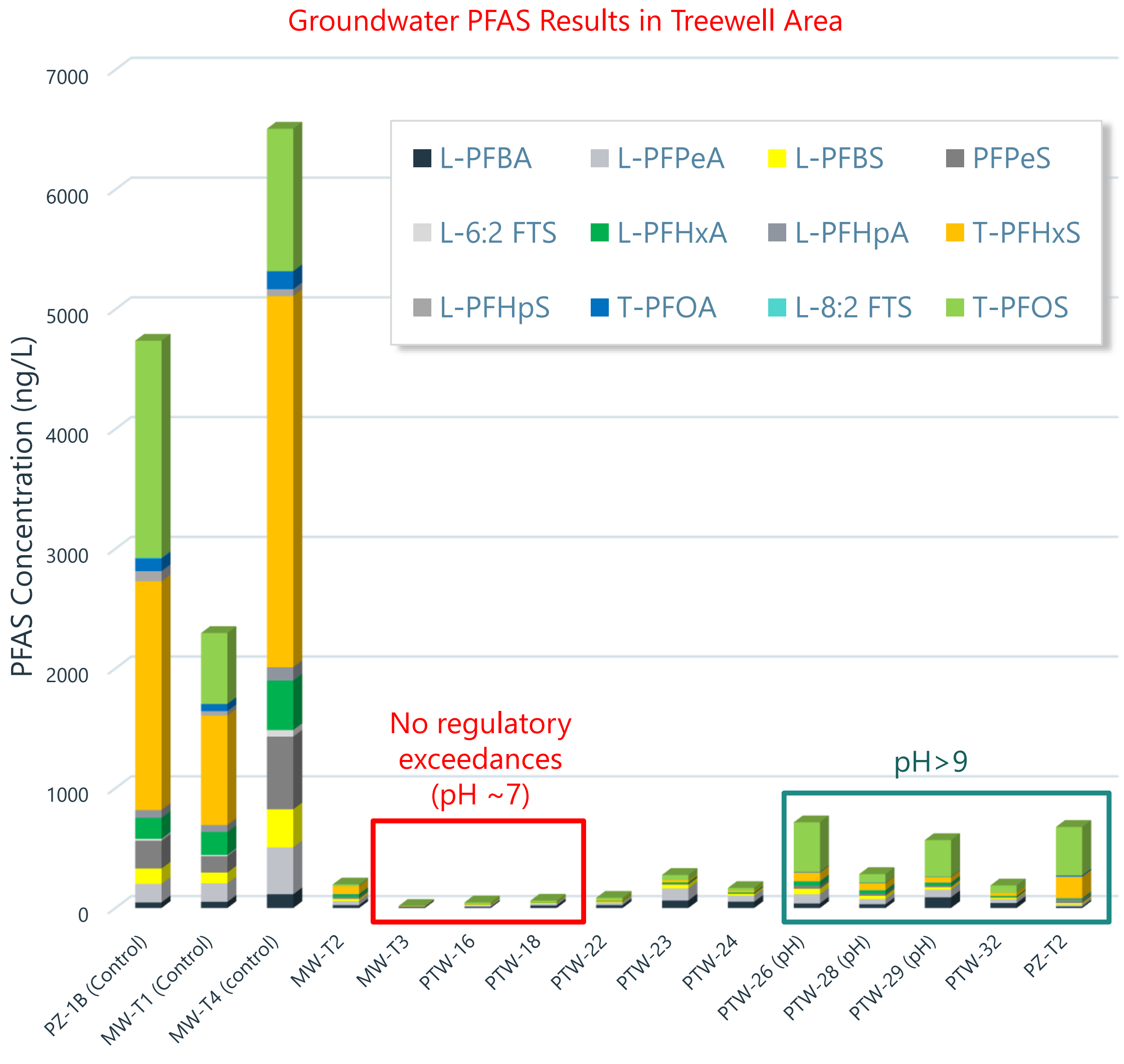
Addressing Storm Water; Adding Source Control – Treewells®

- 2022 – Treewell® Pilot
- BAM™ biochar trenches (2m wide and >3m deep) installed + design investigation in Feb. 2022
- Trees planted April 2022
  - 1m diameter sleeves (>2mbgs)
  - piezometers extend to base of sleeve
  - 10 willows, 18 hybrid poplars and 7 cedars
- O&M ~ monthly in first year



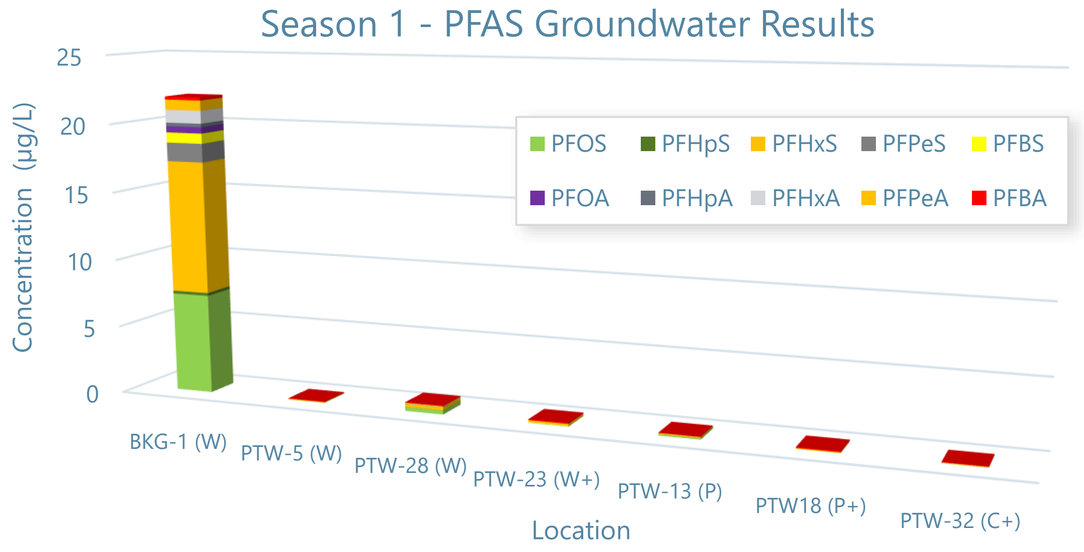
BAM^{TM} Biochar effectiveness - groundwater

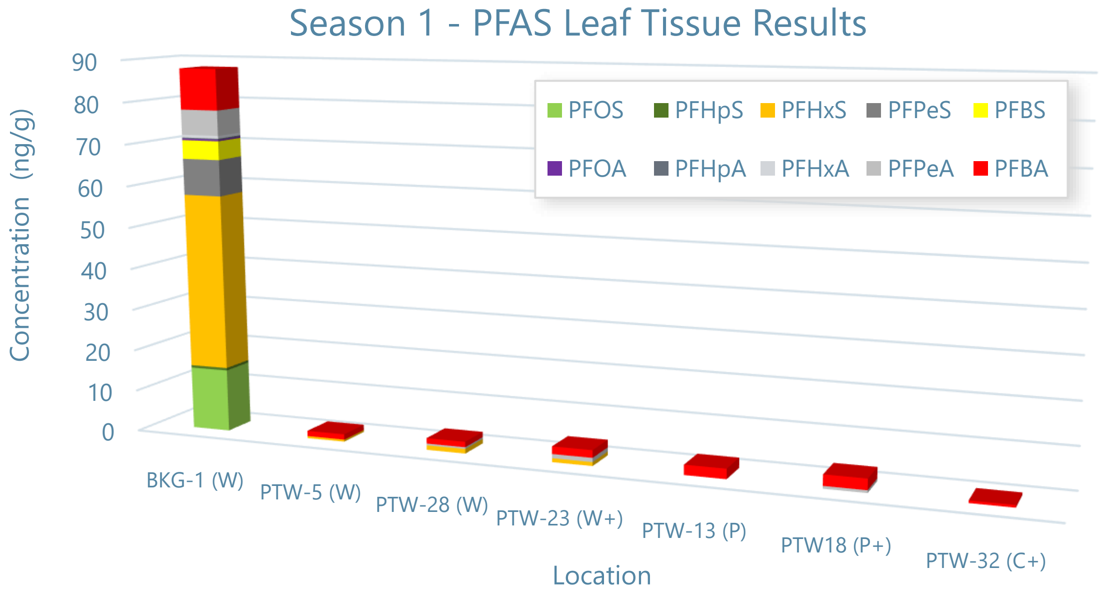
- Samples collected from monitoring/piezometer well network within ~ first month of planting
- BAM^{TM}-related reductions achieving regulatory acceptable PFAS reductions in lower pH (6.5-7.0) portions of the Site
- BAM^{TM} reducing concentrations of short chain PFAS (PFPeA)
- Less sorption observed in area of elevated pH (>9)



Tree uptake – Leaves and Groundwater Results

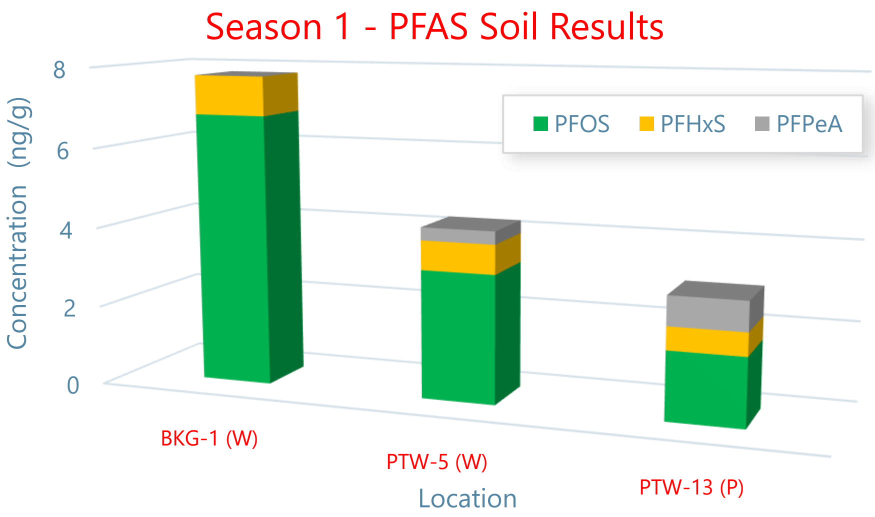
- Piezometers used to collect groundwater samples during plant tissue sample collection
- Full suite of PFAS detected near background tree location sample location
- Background leaf samples shows attenuation of PFOS (long chains) but amplification of PFHxS and shorter chains
- Only PFBA, PFPeA & PFHxS detected in treated treewell leaves (minor amplification)
- Treated groundwater and leaf tissue results ~ equilibrium
- No PFAS detected in “dropped” leaves (not depicted)

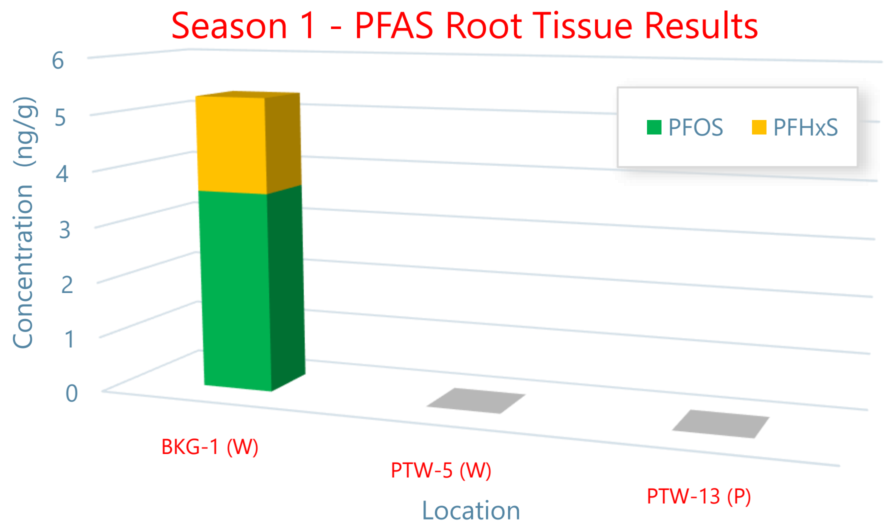




Tree uptake – Roots and Soil Results

- Sept 2022 - wildlife damage
- Two trees were killed and required replacement (i.e., root testing)
- Wild and free willows (~2-3 yrs in age) used for background
- Background tree detected PFOS > PFHxS in soil and root tissue
- BAM™ treated soils detected PFOS > PFHxS ~ PFPeA
- No PFAS detected in treated roots





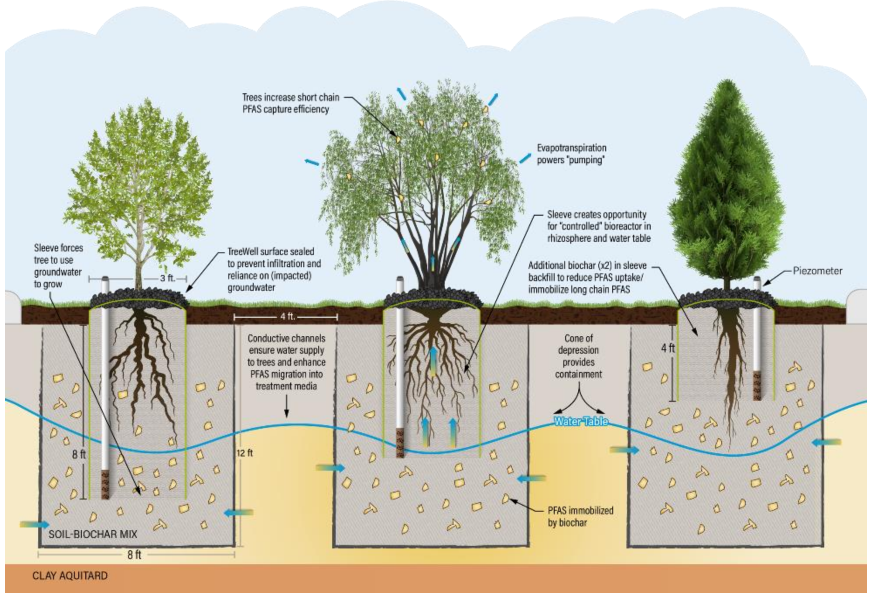
Combining Biochar with Phytoremediation

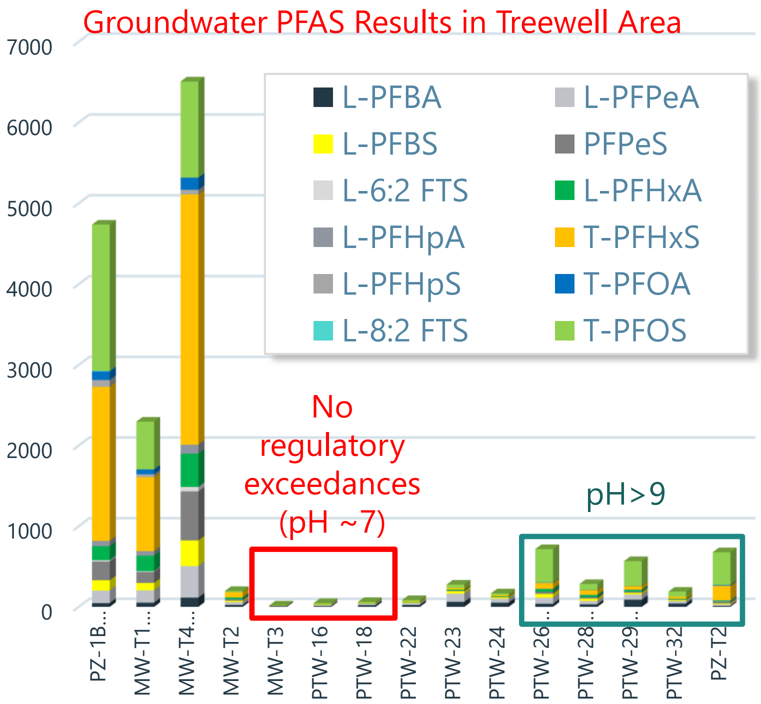
TreeWell systems use groundwater; short chain PFAS magnified in leaf tissue.

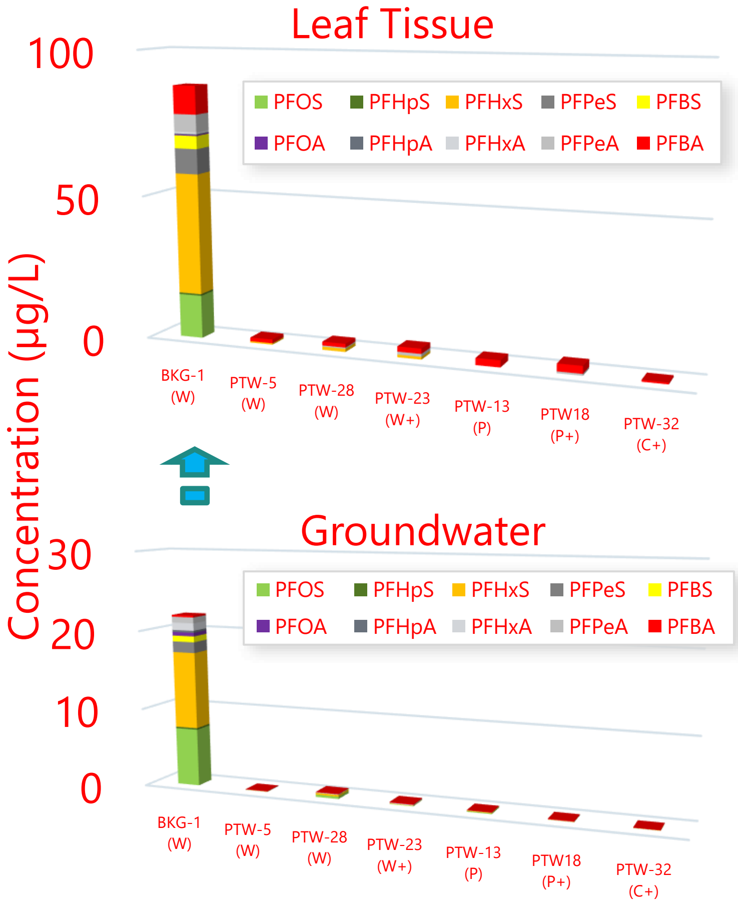
Creates synergy when used with biochar for long chain immobilization.

No PFAS were detected in leaf drop (cycled back into tree with nutrients?).

Roots tend to be in equilibrium with soil.







All results via Mod. Method 537

PFAS treatment via application of biochar in existing infrastructure, engineered systems, soil and groundwater

Summary

Summary – BAM™ Biochar Immobilization

- BAM™ effectively reduced PFAS in groundwater and continues to treat flux
- BAM™ was less effective when installed in existing stormwater infrastructure, likely due to residence time and potential preferential pathways (seams between booms/pillows etc.)
- BAM™ is more cost effective than some other carbon-based immobilization technologies and was not found to be mobile in the formation
- Recycled biomass with lower carbon footprint than other carbon-based approaches
- Finite lifetime for carbon-based sorption capacity?
  - Flux-related rebound occurring in source area groundwater (e.g., PZ-2R).
  - Leaching metrics improved at 1-year+ (esp. sulfonates)
  - Ongoing accumulation of PFAS in biochar at 3+ years
- PFAS “breakthrough” of short chains occurs with carbon

Summary – BAM™ Biochar Immobilization

- Other Considerations?
  - Biochar does sorb precursors
  - PFAS "breakthrough" of short chains occurs with carbon
  - Less sorption efficiency of carboxylates (e.g., PFPeA) over sulfonates (e.g., PFBS)
  - Sorption efficiency decreases under higher pH (e.g, >8)
  - Metals generally not affected. Exception: Local, ~short-term Arsenic

Biochar may also provide niche environment/fresh surfaces for microbial colonization and greater residence time to enhance potential bio-effects.

Wild card at any Site is precursor load (e.g., AOF). PFOS/PFOA may increase with oxygen enrichment (precursor transformation).

Summary – Biochar as an amendment to other technologies

- Biochar effectively reduced uptake of “long chain” PFAS (PFOA, PFOS, PFHxS) into the planted trees
- Treewells add a resilient short chain polish (leafs > shoots/trunks) creating a capture and contain approach with potential for future destruction
- Preliminary sample results suggest that PFAS may be cycled seasonally, akin to nutrients in tree tissues (i.e., in fall, drawn back into the roots)

Thank you!

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