The Promise and Pitfalls of In-Situ Carbon Immobilization of PFAS

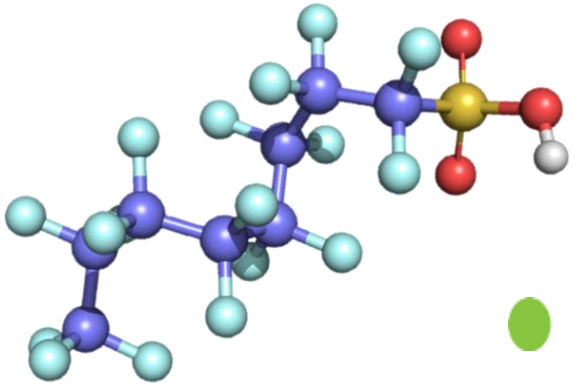
Two Case Studies from Michigan

Len Mankowski – Wood Environment & Infrastructure Solutions
AIPG 2020 PFAS: Beyond the Theoretical and What's Working – Madison, WI

February 27, 2020

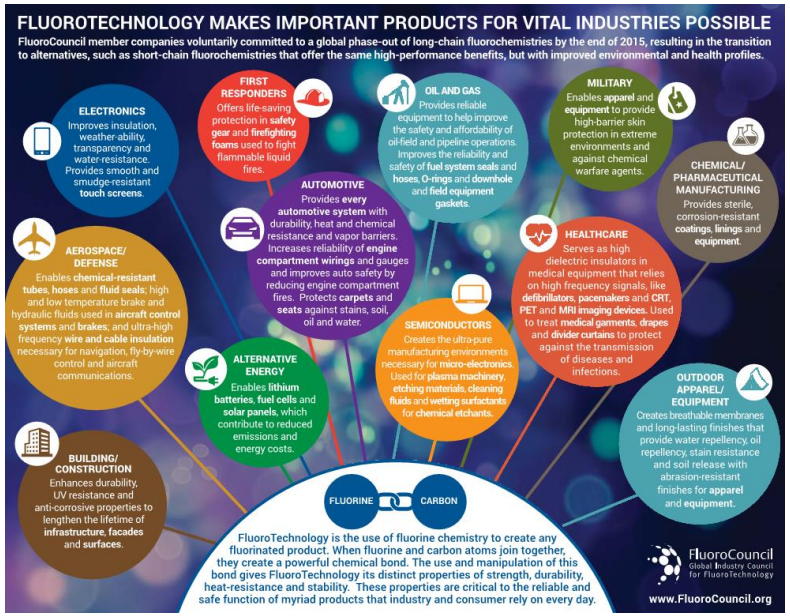
Outline

- Per- and polyfluorinated alkyl substances (PFAS) - Emerging Contaminants of Concern
- Why / Why Not Carbon?
- Injection & Soil Mixing Case Studies – Biochar
- Injection Case Study - Colloidal Activated Carbon
- Summary



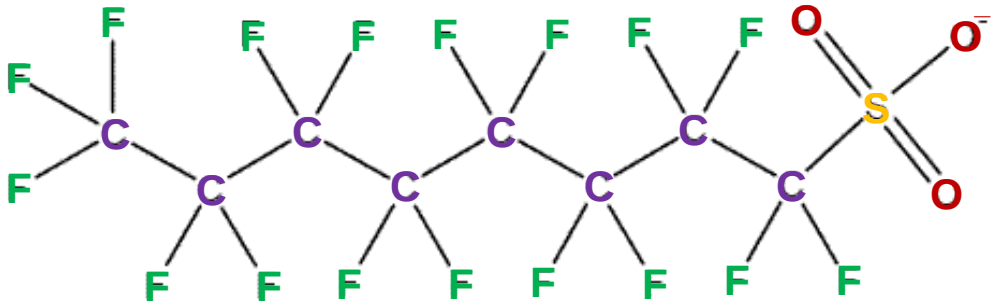
PFAS – Emerging Contaminants of Concern

- Family of over 6000 widely used compounds
- Strong carbon-fluorine bonds
- Persistent in environment
- Surfactants with Hydrophobic “tails” and Hydrophilic “heads”
- Cationic (+), Anionic (-), or Zwitterionic (+ and -)
- Relatively high molecular weight & low volatility



Hydrophobic Tail (Affinity: Air, NAPL, Carbon)

Hydrophilic Head (Affinity: Water)



PFOS - perfluorooctanesulfonic acid

Physical and Chemical Properties of PFAS

Compound	Acronym	Number of Carbon Atoms	Solubility, g/L at 25ºC (Concawe 2016)	Log Koc (USNLM 2017)
Perfluorooctanesulfonic acid	PFOS	8	0.52 – 0.57	2.4 – 4.7
Perfluorohexanesulfonic acid	PFHxS	6	2.3	1.78
Perfluorobutanesulfonic acid	PFBS	4	46.2 – 56.6	2.26
Perfluorononanoic acid	PFNA	9	9.5	5.08
Perfluorooctanoic acid	PFOA	8	3.4 – 9.5	1.92 – 2.59
Perfluoroheptanoic acid	PFHpA	7	4.2	1.52 – 2.82
Benzene		6	1.8 @ 20º C	2.15
Trichloroethylene	TCE	2	1.1 @ 20º C	2.42

~ Smaller chains tend to be more soluble in water
~ Longer chains tend to have higher organic carbon partitioning coefficients (Koc)
~ Variation based on functional groups

PFAS – Risks and Screening Levels (Michigan)

- Bioaccumulate
- EGLE has established criteria for PFOA and PFOS in multiple media
- EGLE proposed drinking water health based values (HBVs) for five+ compounds

PFAS	EGLE Drinking Water	HBV Drinking Water[1]	EGLE Surface Water[3]
PFBS	--	420	--
PFHxS	--	51	--
PFOA	70[2]	8	12,000
PFOS	70[2]	16	12
PFNA	--	6	--

[1] Health based values for drinking water in public comment (2019).

[2] Individually or combined PFOA + PFOS (2018)

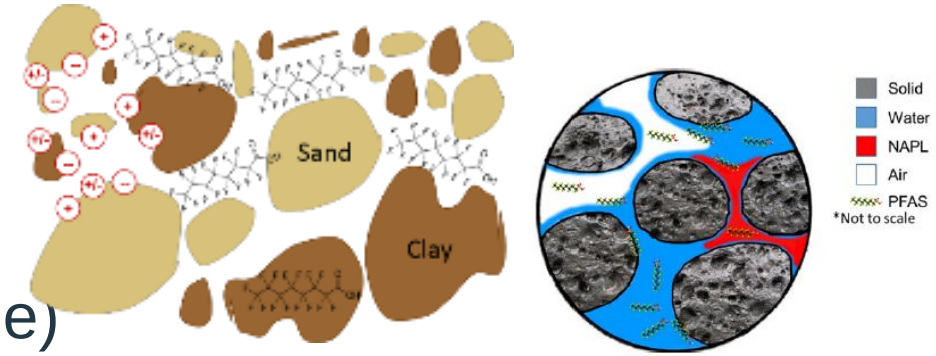
[3] Surface water not used as human drinking water source (non-drink)

All concentrations in nanograms per liter (ng/L)

PFAS Fate and Transport in Soil – Wood Portfolio Study

PFAS Fate & Transport - Conceptual:

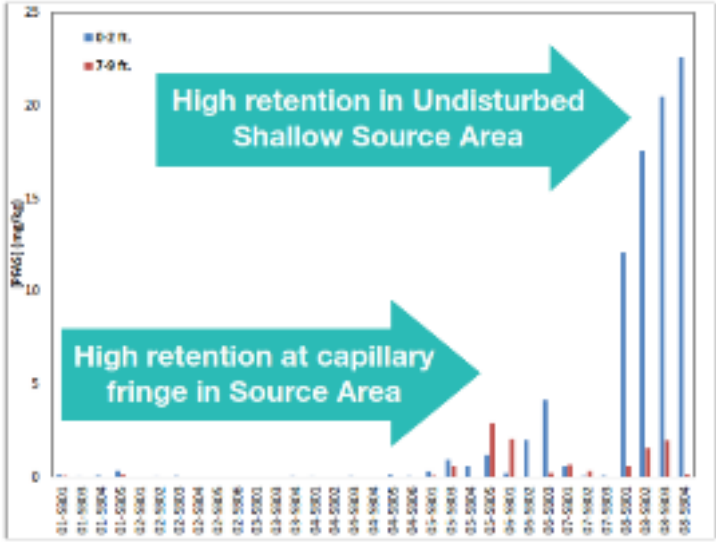
- F&T is <u>site-specific</u>
- Source distribution
- Retention at air-water interface (capillary fringe)
- Interaction with other contaminants (e.g. NAPL)
- Transformation (oxidation conditions)
- Biologically resistant to attenuation



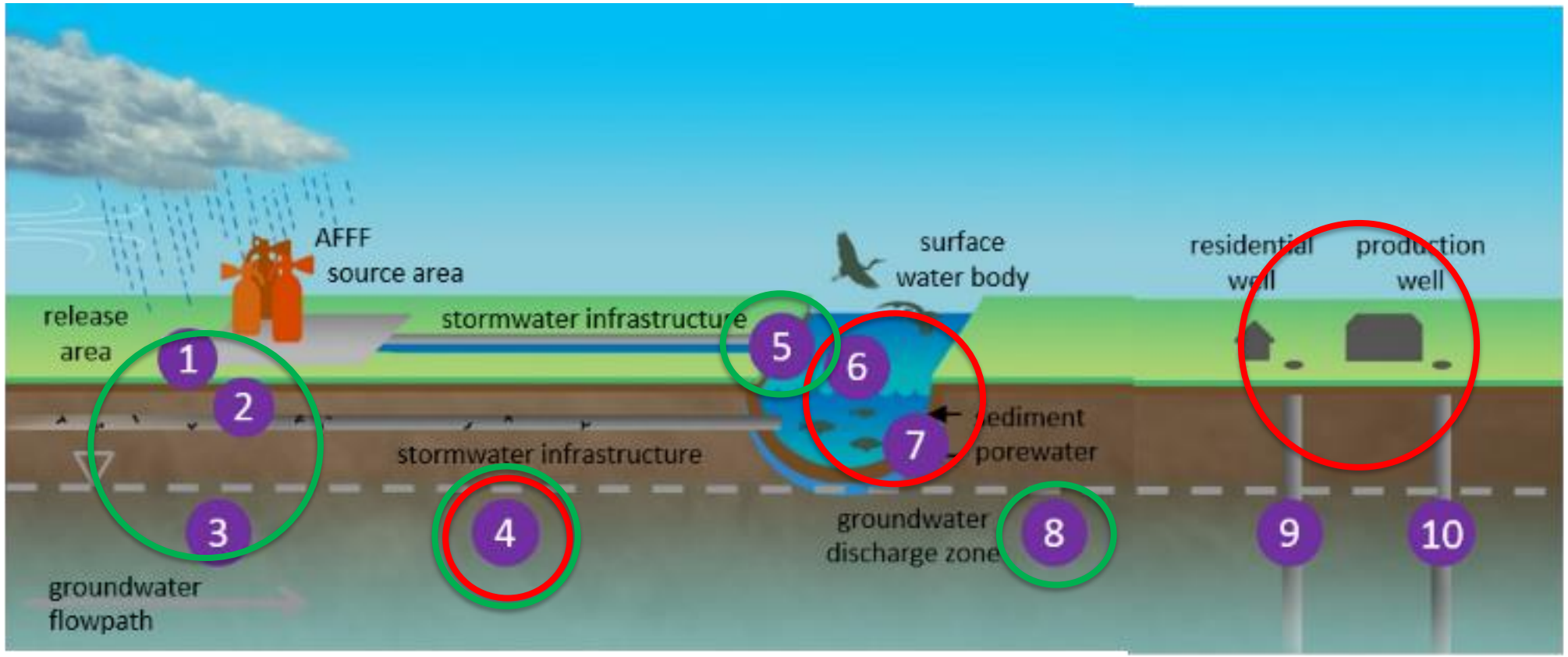
Brusseau, M. L.; 2018 - Science of the Total Environment; 176-185

Factors Influencing Retention:

- Cationic/Anionic Exchange Capacity (CEC/AEC)
- pH
- Total Organic Carbon (TOC) and Clay Content (?)
- What you have - long chain PFAS (≥6 C) generally sorb more readily



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

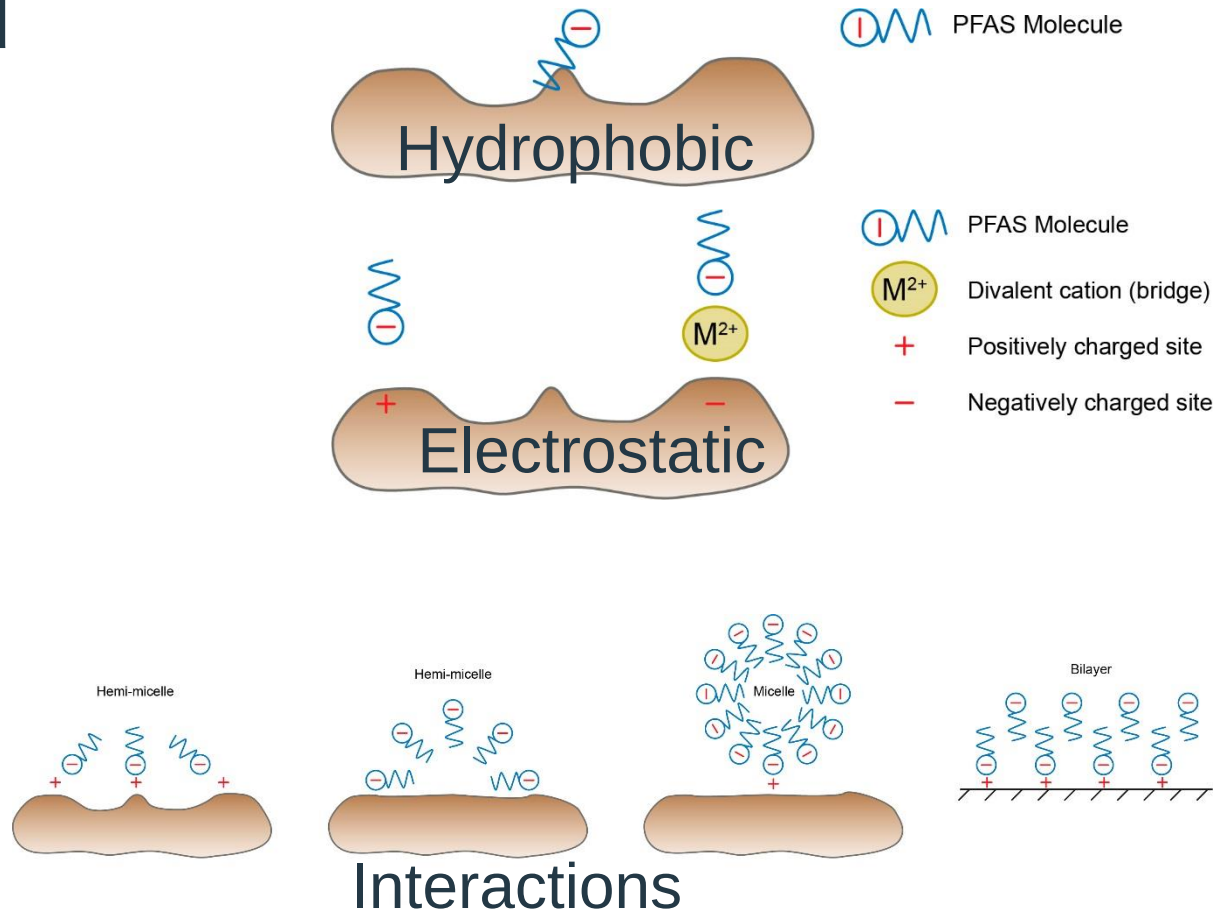
PFAS – Why Carbon?

Cost effective remediation tools needed

Carbon:

- Proven ex-situ treatment
- Proven Injectable technology
- High microporosity & surface area:volume ratio
- Enhance TOC - Adsorption via hydrophobic tails
- Enhance CEC - Sorption via electrostatic interactions with hydrophilic head

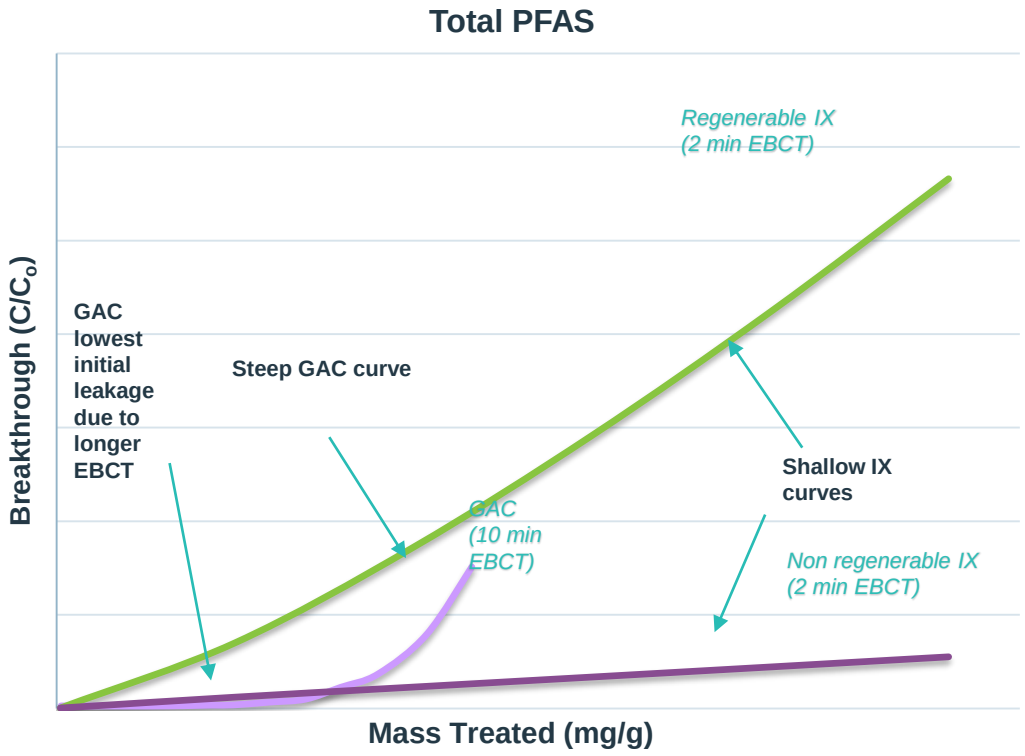
Retain now – Destroy later?



Modified from Z. Du et al 2014

PFAS – Why Not Carbon?

- Retention <u>is not</u> Destruction
- Finite Lifetime for Carbon…Rejuvenate, Remove?
- PFAS “Breakthrough” varies & steep curve
- Sorptive capacity?
- Site Specific Influences?
- Biofilms?
- Kinetics / competition:
  - Other PFAS?
  - Other Site COCs?
- Particulate Delivery / Contact

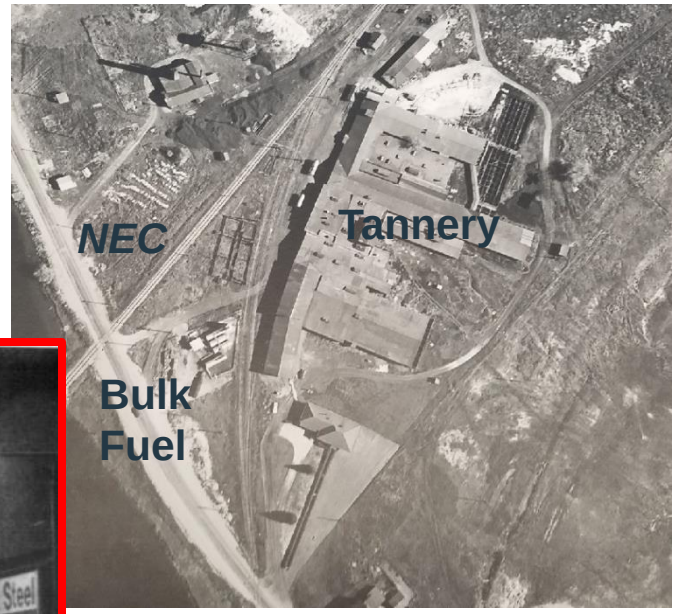


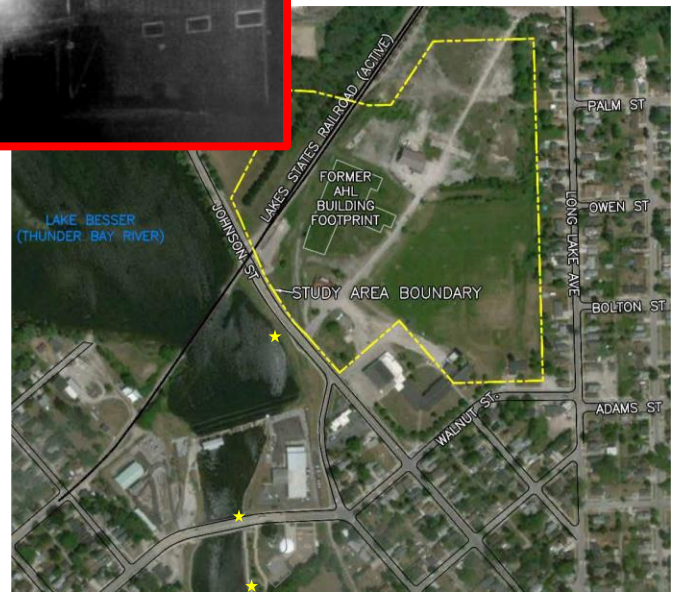
Case Study – BioChar Injection & Soil Mixing Pilots at a former Tannery

- Site Setting/History
- Conceptual Site Model
- Brief Description of Pilot Tests
- Performance Metrics

Alpena Hide and Leather – Site History

- Tannery & Tannin producer (NEC) ~1895 - 1952
- Sinclair Bulk Fuel Terminal ~1930-1955
- Post Tannery – Warehousing & Light Manufacturing
- Fire – October 2005
- Current Use:
  - Storage units
  - Brewery
  - Soccer fields





Site Specific Considerations

- Filled Lowland; granular fill over outwash/fluvial sand; lenses of organic silt
- Unconsolidated aquifer extending to 7-15 ft; Depth to water: 0-5 ft
- Silt-rich till separates unconsolidated aquifer from Limestone (Traverse Group)
- Organic carbon (f_{oc}) ~ 0.02 – 1.9% (Walkley Black)
- Advective groundwater flow rate ~0.56 feet per day (K~1.3 – 23 ft/day)
- Source area aquifer conditions:
  - Anaerobic (ORP: -350 to -150 mV) transitions to aerobic
  - Variable pH (pH: 6.5-9.5)
  - Groundwater TOC ~ 16 mg/L (geomean); (91 mg/L in organic silt)
  - CEC ~ 3.4-6.5 meq/100g soil (Ca^{+2}>>Mg^{+2}~Na^{+1}> K^{+1})
  - Chlorides ~ 110 mg/L (average)

Non-PFAS Contaminants

- **Soil**

  Arsenic

  Residual petroleum

  Residual Hide material

- **Groundwater**

  Chlorides

  Arsenic “Plume”

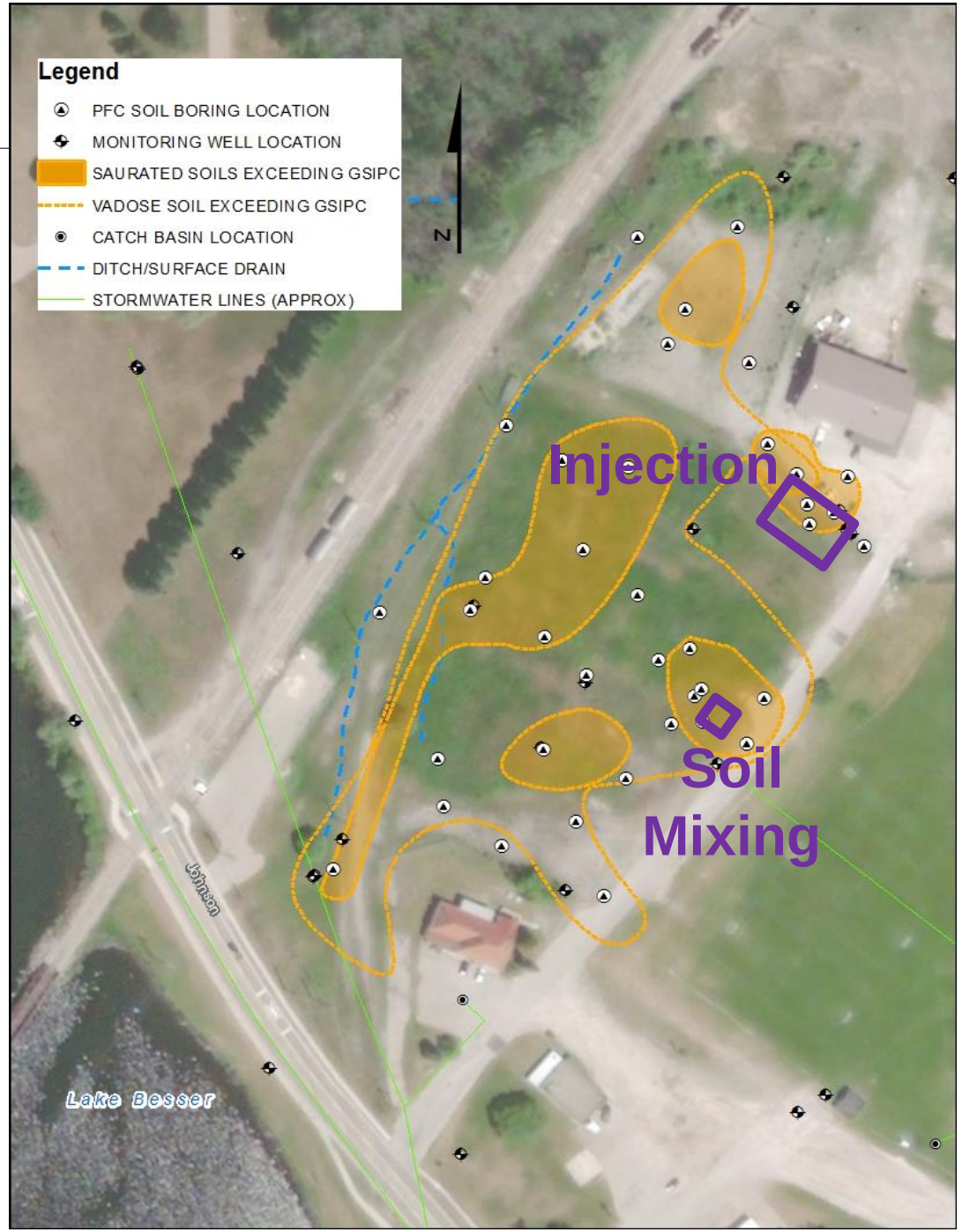
  Other metals (e.g., Pb, Cr^{+3}, Cu)

  +/- Cyanide

- **PFAS Detected in Groundwater in 2017**

PFAS in Soil

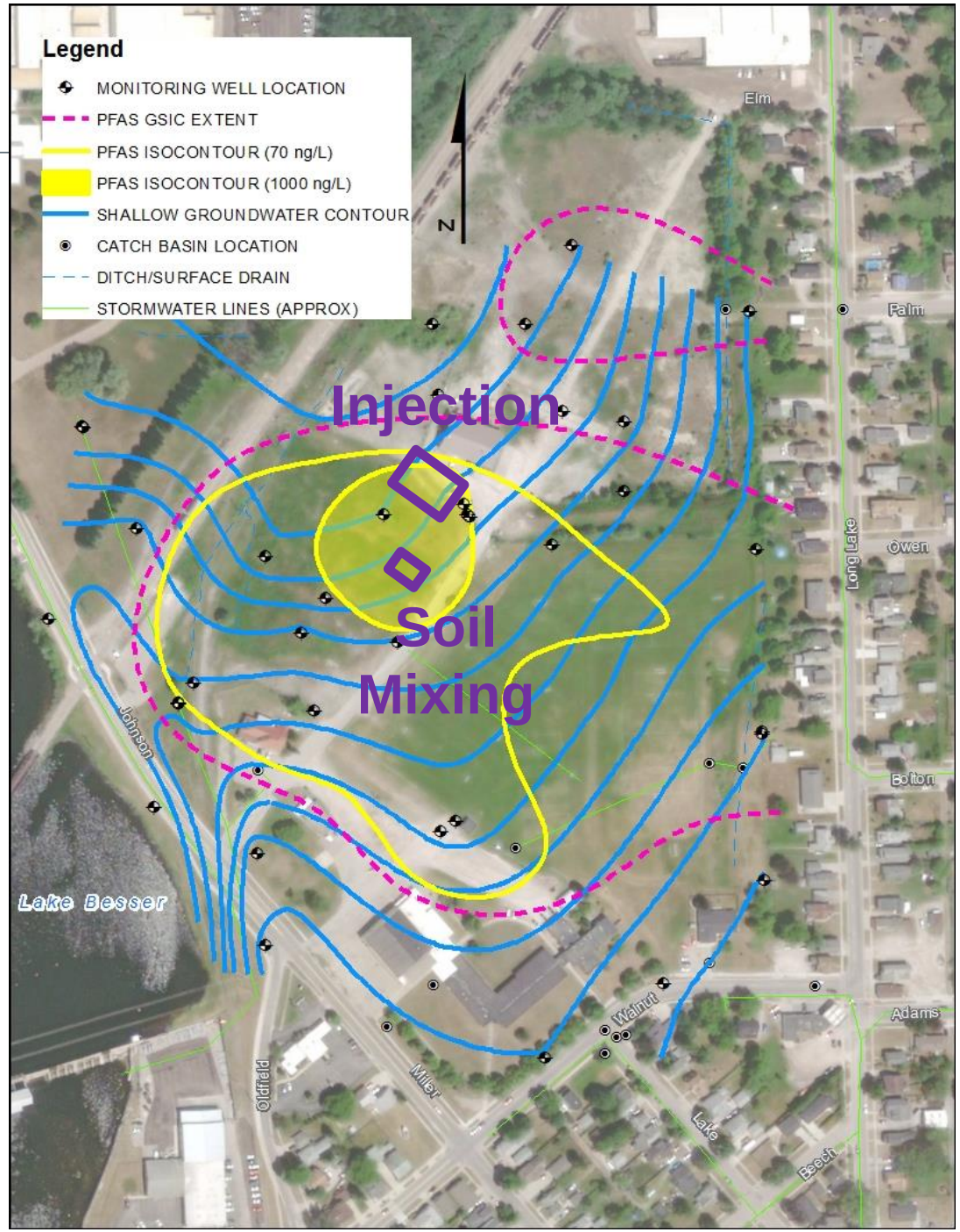
- 14 Different PFAS have been detected
- PFOS and PFHxS highest frequency of detections
- Widespread at 1.5’ (Cap Fringe)
- Hotspots at 4-5 feet; extend along topographic lows
- PFOS up to 264 ng/g
- PFHxS up to 43 ng/g
- PFOA up to 5.4 ng/g (<10%)



PFAS in Groundwater

- 16 Different PFAS have been detected
- Detections in 95% of samples collected (n=264)
- Perfluorobutanoic acid (PFBA) highest individual frequency (92%)
- PFOS as high as 5420 ng/L

  161 detections > 12 ng/L
- PFHxS as high as 10,800 ng/L
- PFOA up to 804 ng/L (85%)



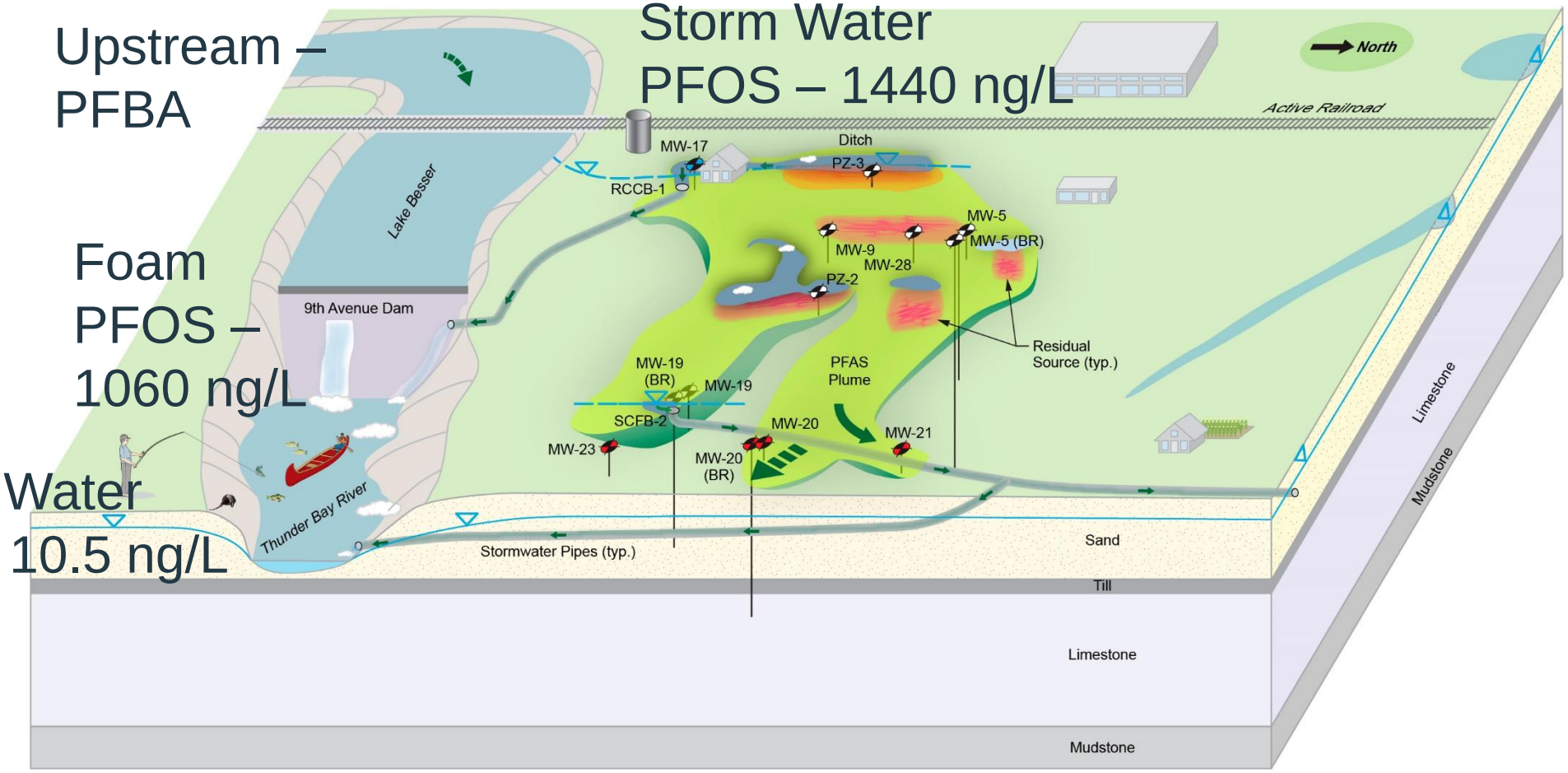
Alpena Hide and Leather – Conceptual Site Model

Upstream –
PFBA

Storm Water
PFOS – 1440 ng/L

Foam
PFOS –
1060 ng/L

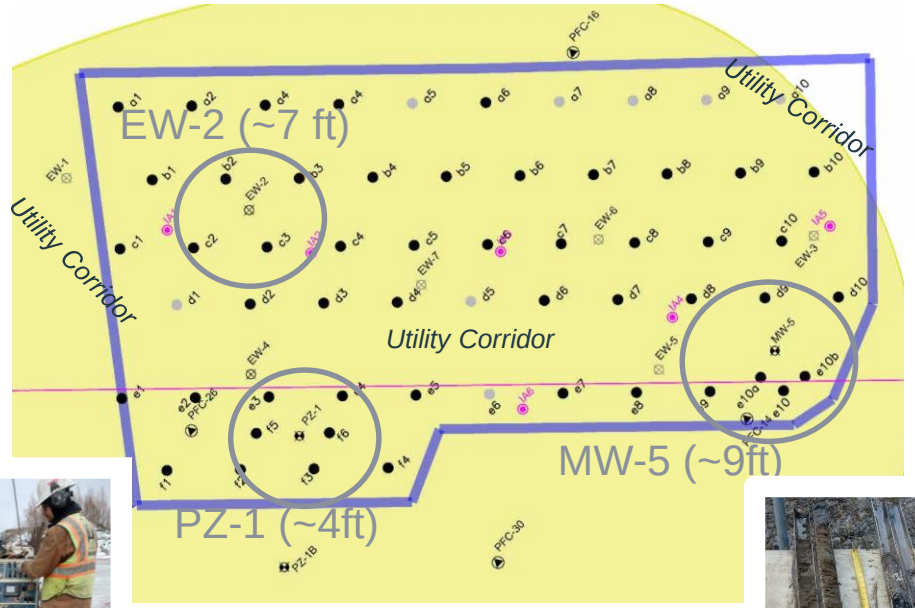
Surface Water
PFOS – 10.5 ng/L

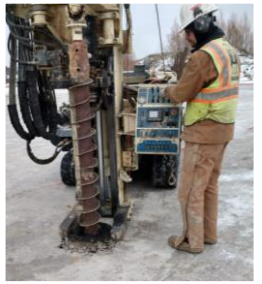


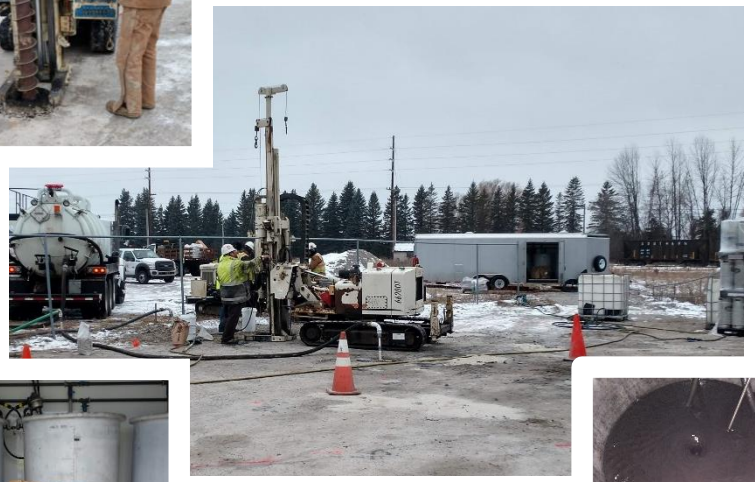
Not To Scale

December 2018 Biochar Injection Pilot Test

- Location: utilities & planned for paving
- Injection completed with ORIN Remediation using 30 µm BAM-Ultra™
- Solid media mixed in treatment trailer
- 46 Injection locations (typ 7-ft centers, Area of ~30-ft by 75-ft)
- Bottom up Injection (2-ft lifts, 2-10 ft bgs)
- 100 gallons of 12.4% BAM-Ultra™ Solution Injected at each location (5300 pounds)
- **Push -** Injection pressures of 40 – 100 psi
- **Pull -** Vac Truck, 7 extractions wells + existing wells. 8,400 gallons of liquid waste (Treated in frac tank with BAM-X™)

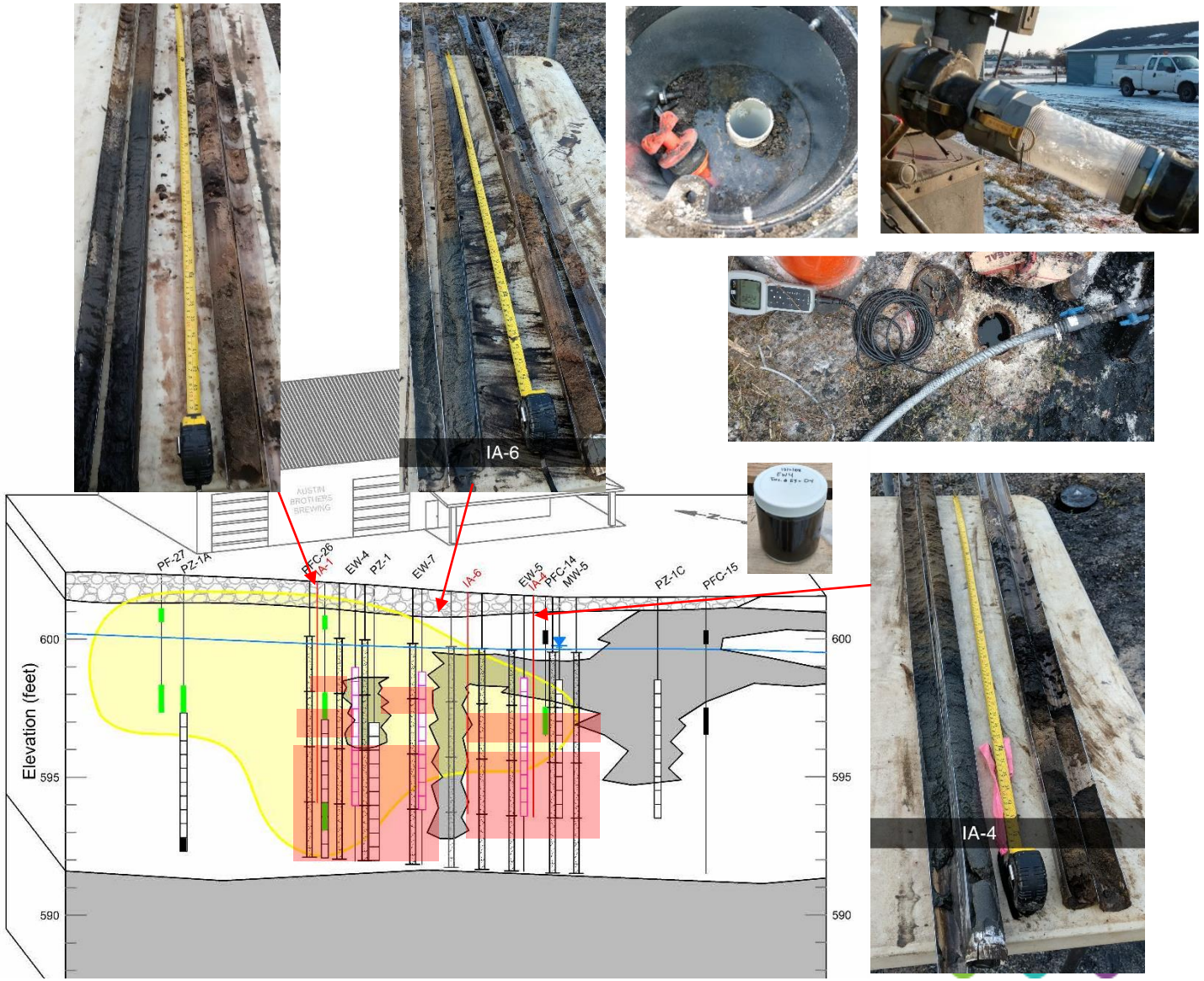






Distribution/Radius of Influence

- Confirmation Soil Borings
- Visual evidence in borings at 2.5-5 ft from inject/extract locations
- Heterogenous vertical distribution in cores – *Primary Injection Interval 4-8 ft bgs*
- Well Network Monitoring:
- Mounding & conductivity changes
- Direct connection to extraction wells at 4-5 ft bgs



Alpena Hide and Leather – Soil Mixing Pilot Test

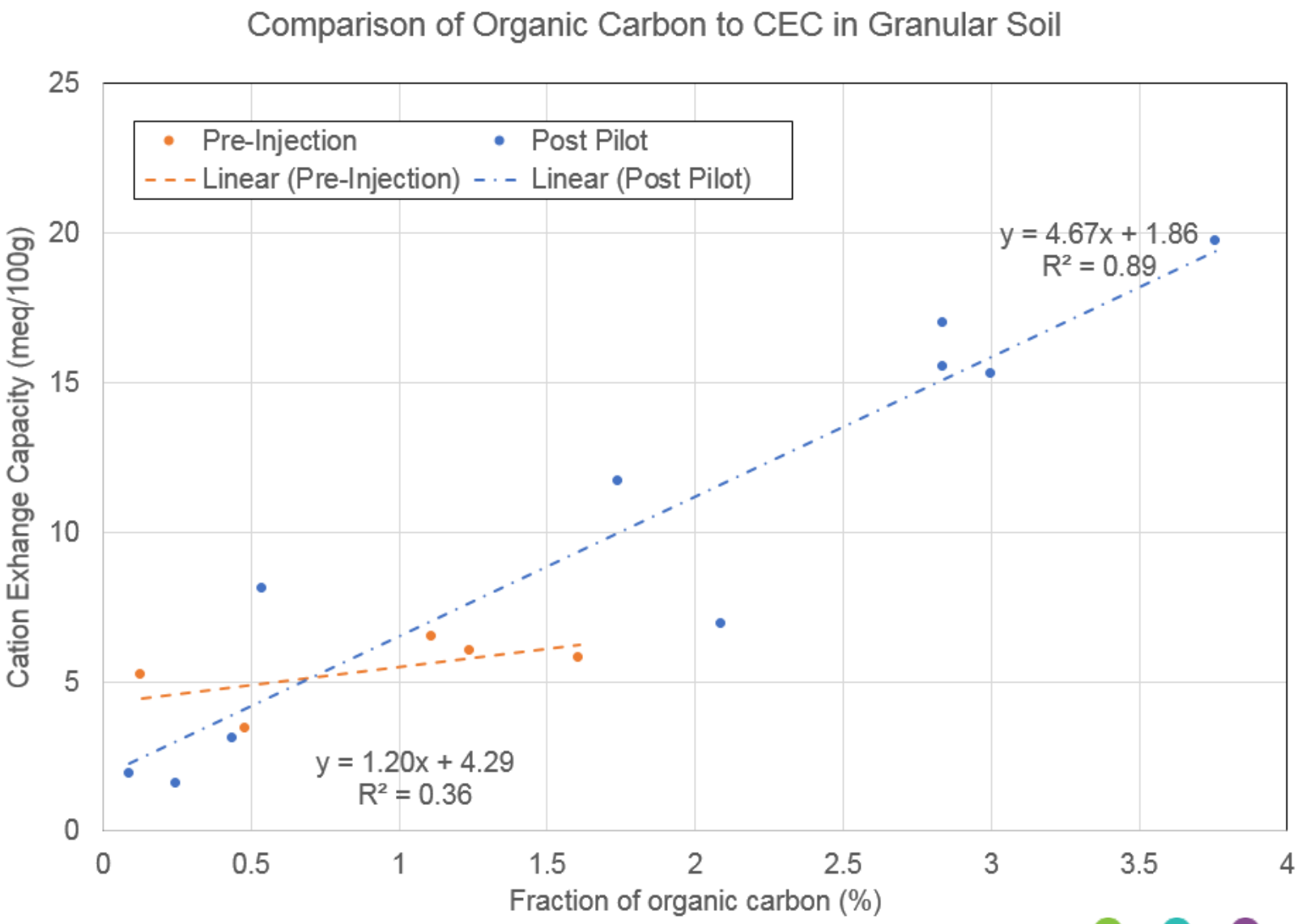
- Location – Future buildout
- Excavator, skid steer & Super Sack
- 1600 pounds of BAM-XTM Mixed into 800 cf

  ~1.5% loading

  Mixed in place, no waste generated
- Post mixing cores - ~homogeneous (3 of 4)

Alpena Hide and Leather – Soil Results

- CEC and f_{oc} increased over baseline after injections
- The CEC:f_{oc} ratio in soil increased after treatment



Leaching Results

- Soil SPLP/TCLP Analysis (Modified Method 537) at post and 1 year
- **Soil Mixing (Decreased at 1 yr):**

  PFOS SPLP & TCLP - 27 ng/L & 8.2 ng/L

  Tot. PFAS SPLP & TCLP 54 ng/L & 57 ng/L
- **Injection Area (Decreased at 1 yr):**

  PFOS SPLP & TCLP 34-61 ng/L & 17-64 ng/L

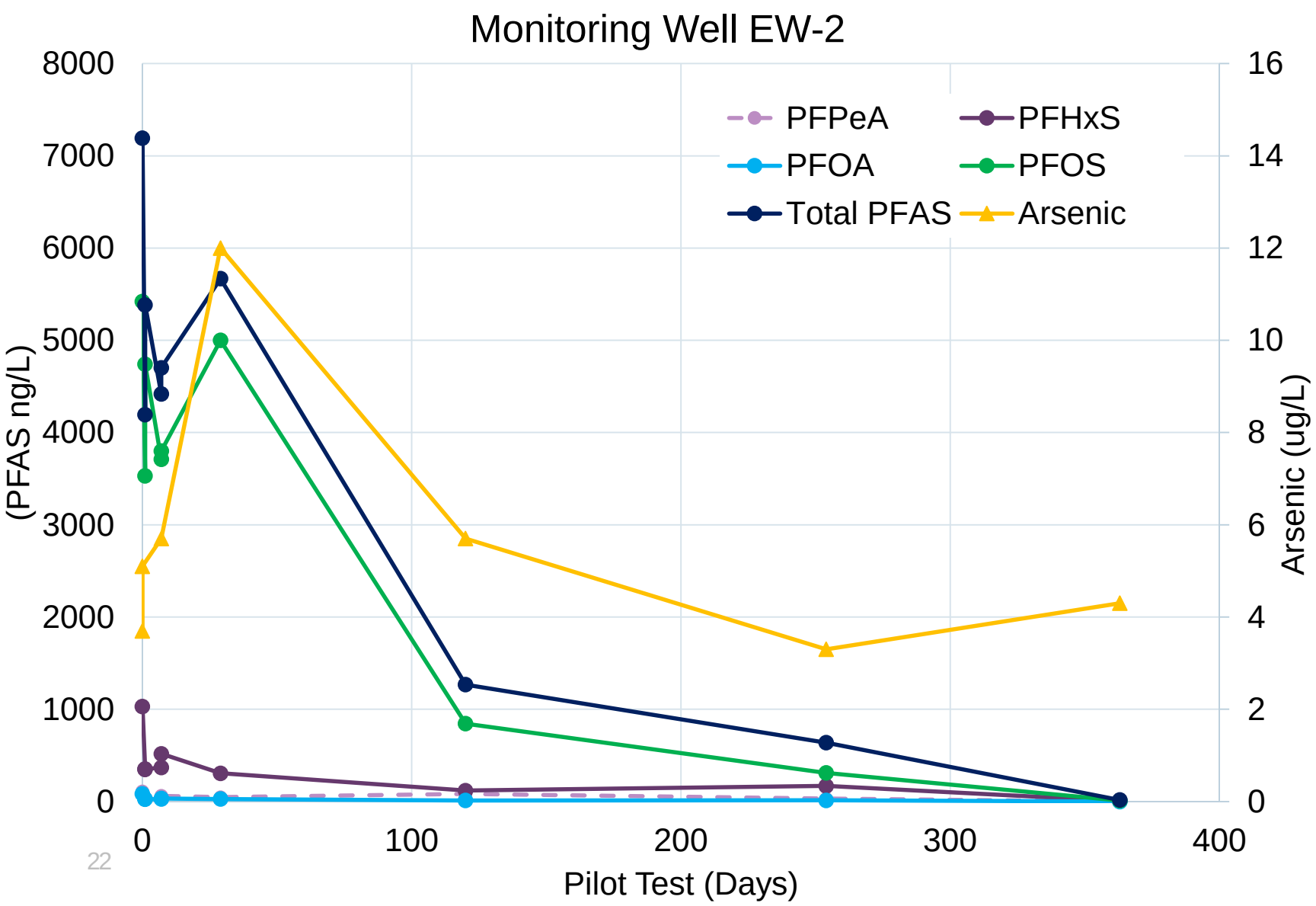
  Tot. PFAS SPLP & TCLP 46-169 & 29-88 ng/L

Results confirm visual observation of media present to SPLP/TCLP reductions.

Test	PFAS	BL	Injection Area	Soil Mixing
SPLP	PFPeA	5.14	ND-3.1 (40 to 100%)	ND-6.7 (-12 to 100%)
SPLP	PFOS	117	34-190 (-17 to 73%)	27-36.3 (69-77%)
SPLP	Total	171	45.9-200 (-19 to 73%)	54.3-74.1 (57 to 68%)
TCLP	PFPeA	7.7	ND-3.70 (52 to 79%)	4.73-9.12 (-78 to 39%)
TCLP	PFOS	414	17-200 (52 to 96%)	8.2-48.4 (88 to 98%)
TCLP	Total	568	29.3-233 (59 to 95%)	35.7 (95%)

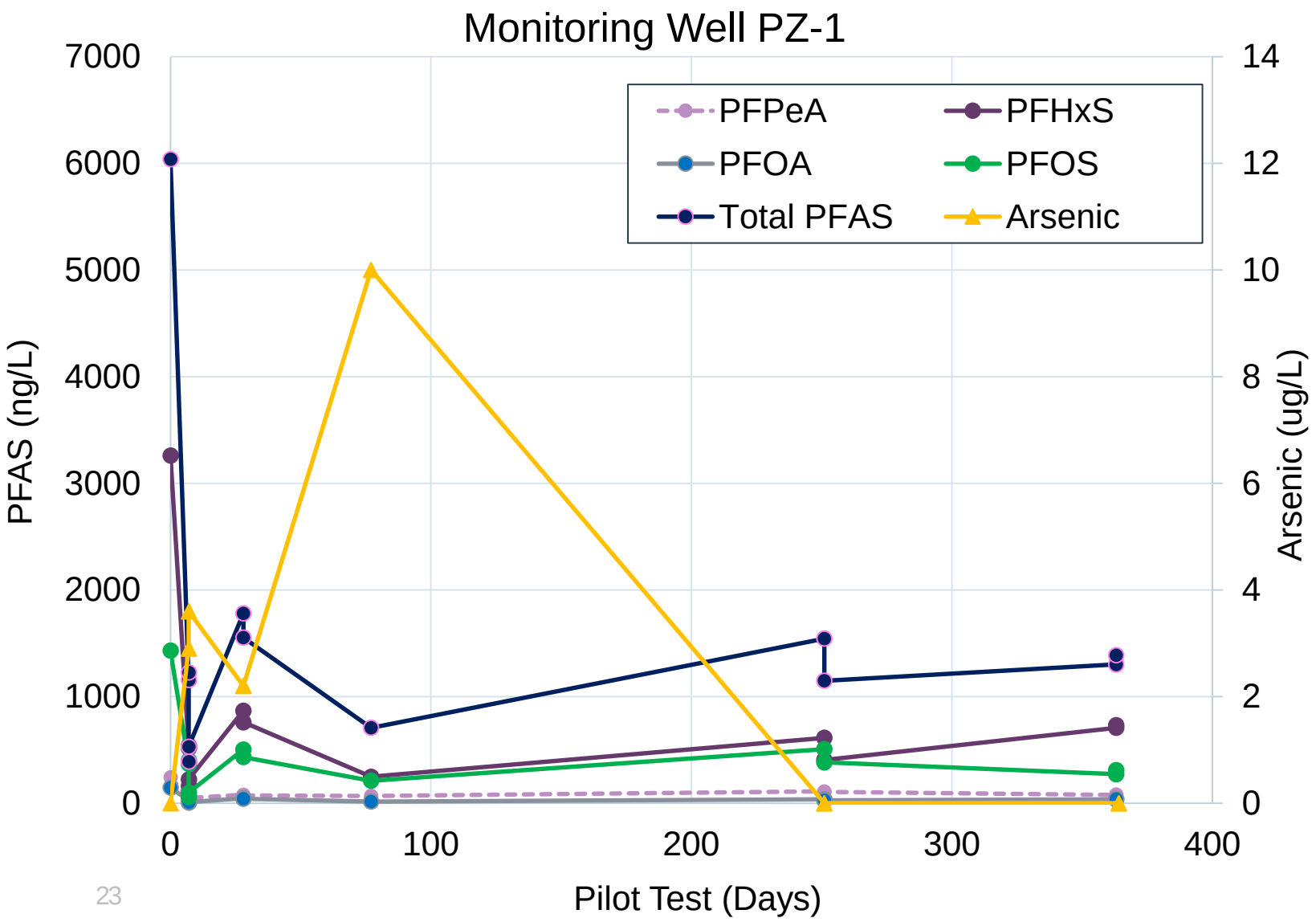
Leachate results in ng/L (percent reduction)

Groundwater Results – 7-ft Injection Array (~0.6% Loading Rate)



PFAS		Percent Reduction
PFCA	PFBA	96
	PFPeA	ND
	PFHxA	ND
	PFOA	ND
PFSA	PFBS	ND
	PFHxS	99.5
	PFOS	99.8
	8:2FTS	ND
T-PFAS		99.8

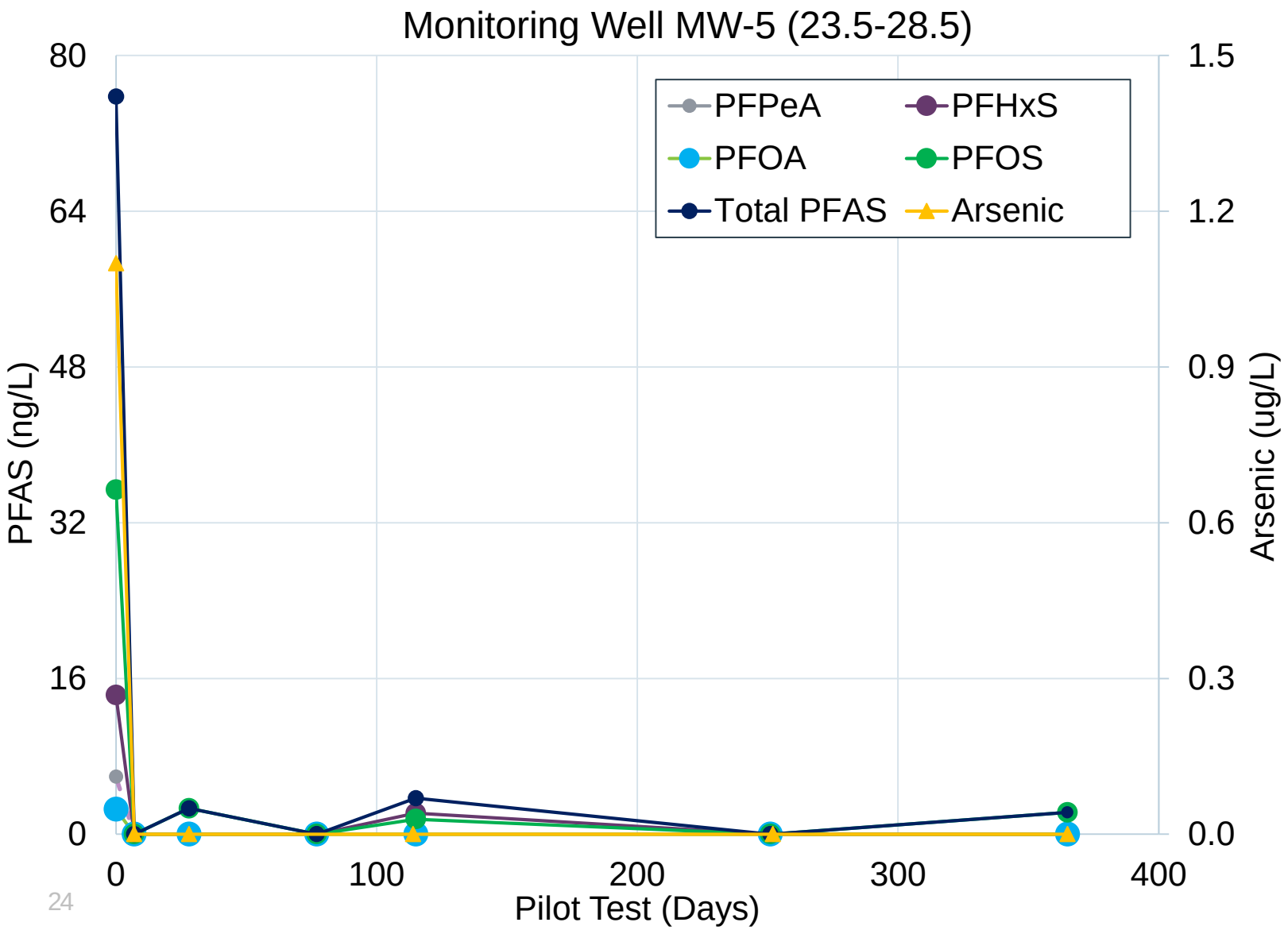
Groundwater Results – 4-ft Injection Array (~1% Loading Rate)



PFAS		Percent Reduction
PFCA	PFBA	58
	PFPeA	67
	PFHxA	82
	PFOA	74
PFSA	PFBS	75
	PFHxS	78
	PFOS	80
	8:2FTS	100
T-PFAS		78

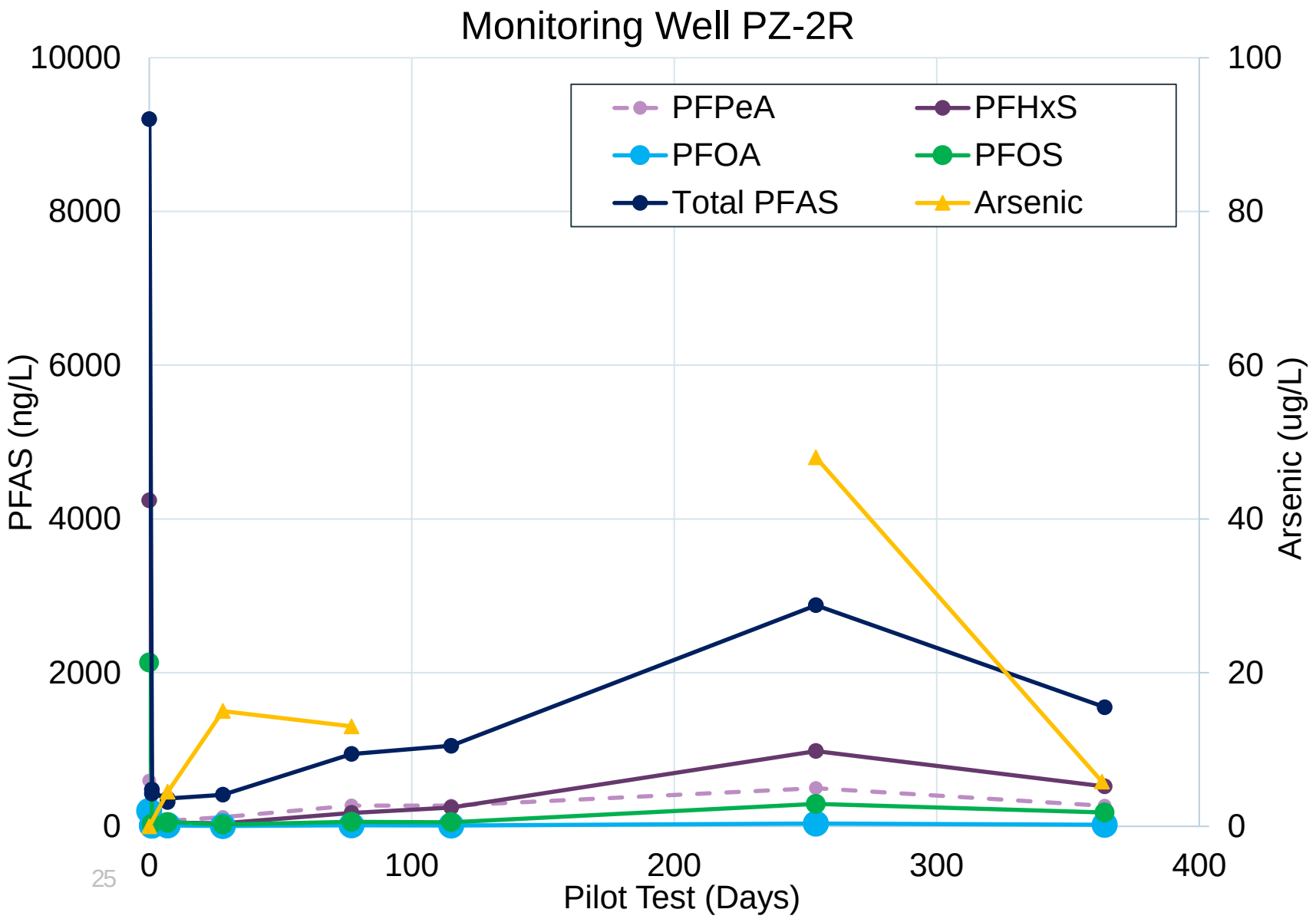
- Hydraulic Conductivity
  Pre-Test = 11 ft/day
  Post Test = 8.0 ft/day

Groundwater Results – Bedrock (Below Injection Area)



PFAS		Percent Reduction
PFCA	PFBA	ND
	PFPeA	ND
	PFHxA	ND
	PFOA	ND
PFSA	PFBS	ND
	PFHxS	ND
	PFOS	94
	8:2FTS	ND/ND
T-PFAS		97

Groundwater Results – Soil Mixing Area (1.5% Loading Rate)



PFAS		Percent Reduction
PFCA	PFBA	39
	PFPeA	55
	PFHxA	85
	PFOA	90
PFSA	PFBS	57
	PFHxS	88
	PFOS	92
	8:2FTS	ND
T-PFAS		83

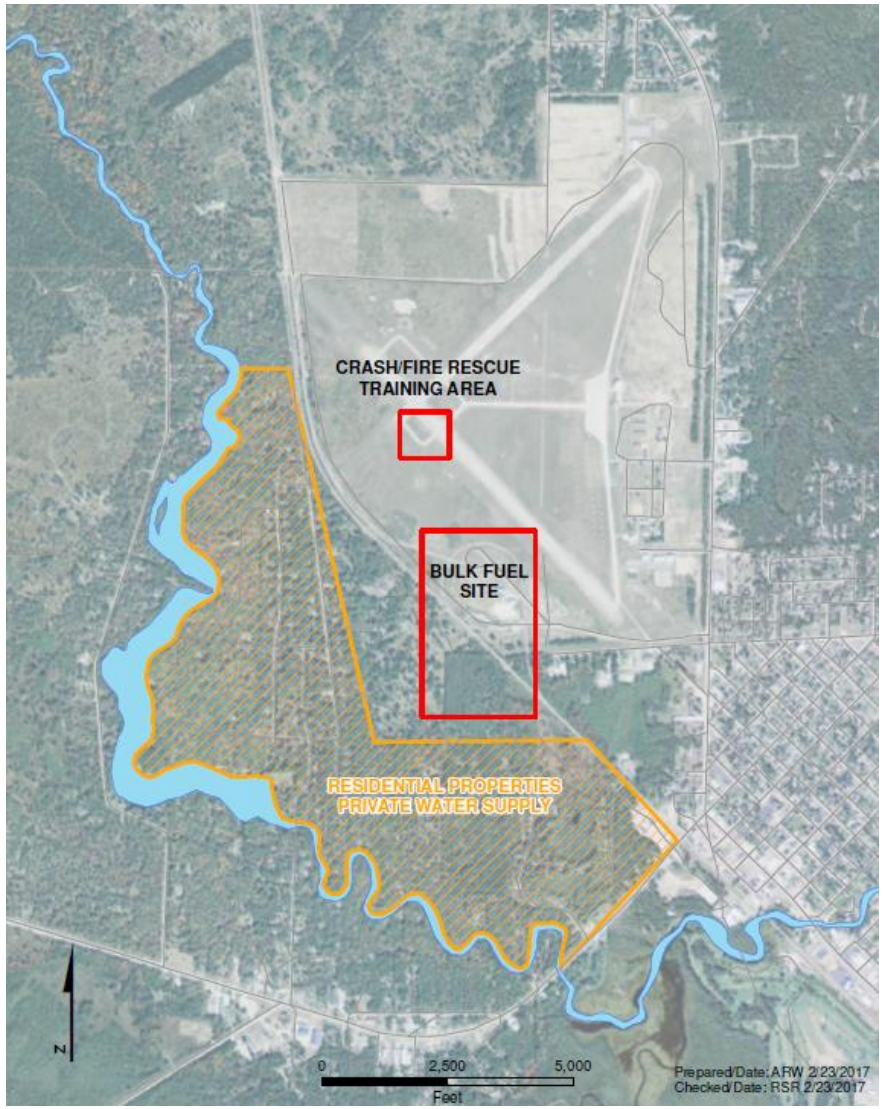
- Hydraulic Conductivity
  Pre-Test = 11 ft/day
  Post Test = 0.9 ft/day

Case Study – Colloidal Activated Carbon in a Low Centration PCE Plume

- Site Setting
- Conceptual Site Model (Injection Area)
- Brief Description of Pilot Test
- Performance Metrics / Mechanisms

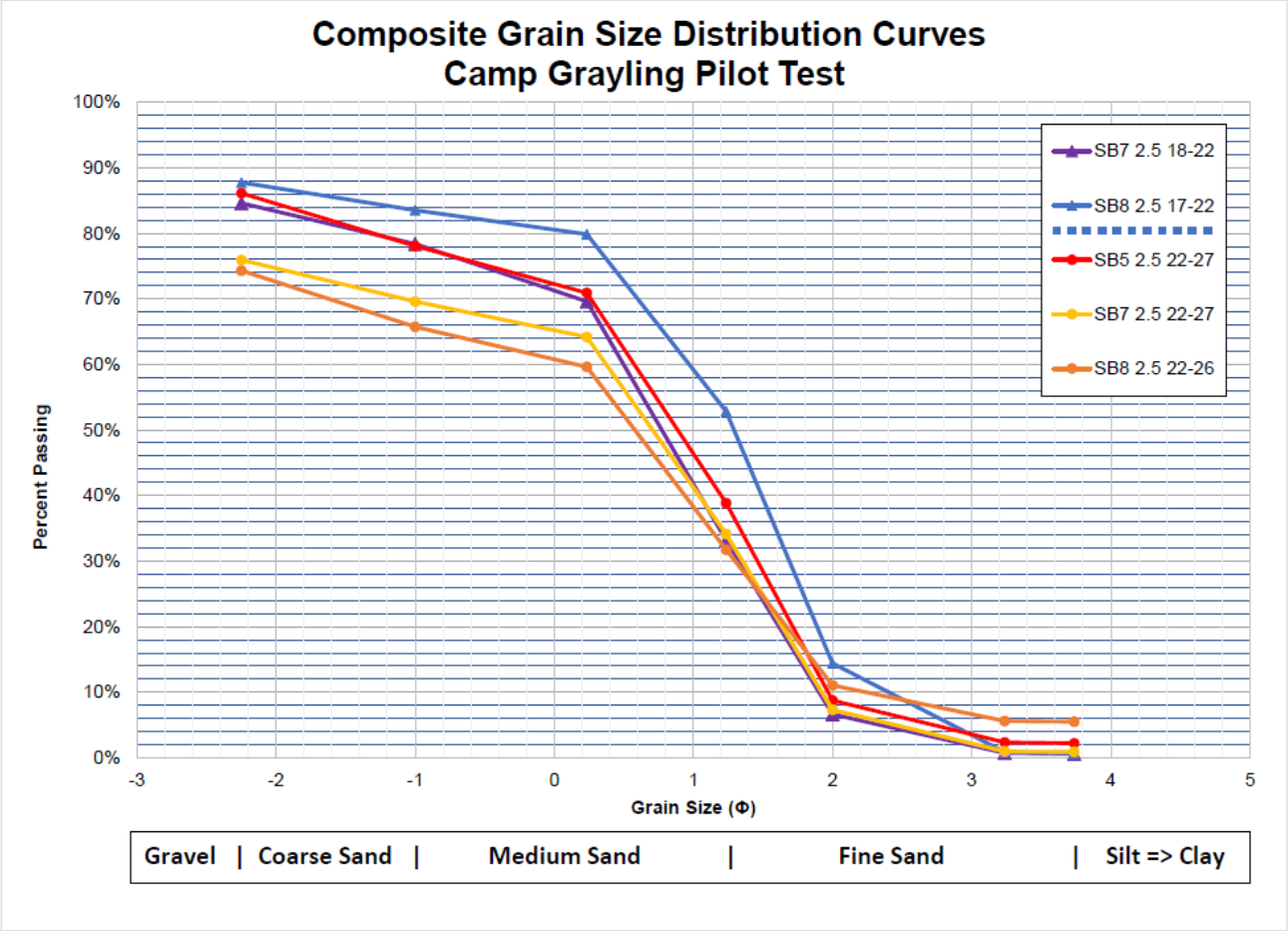
Camp Grayling Airfield – Conceptual Site Model

- Former Fire Training Area
- Bulk Fuel Area
  - Pump and Treat System in Place
  - Previous HRC Injections
- Compounds in groundwater
  - Historically SVOCs
  - Low Level PCE (<10 ug/L)
- PFAS Detected 2016
- PFAS characterized via Outside-In Approach (Receptor based)
- Vertical Aquifer Profiling in 2016 defined vertical extent



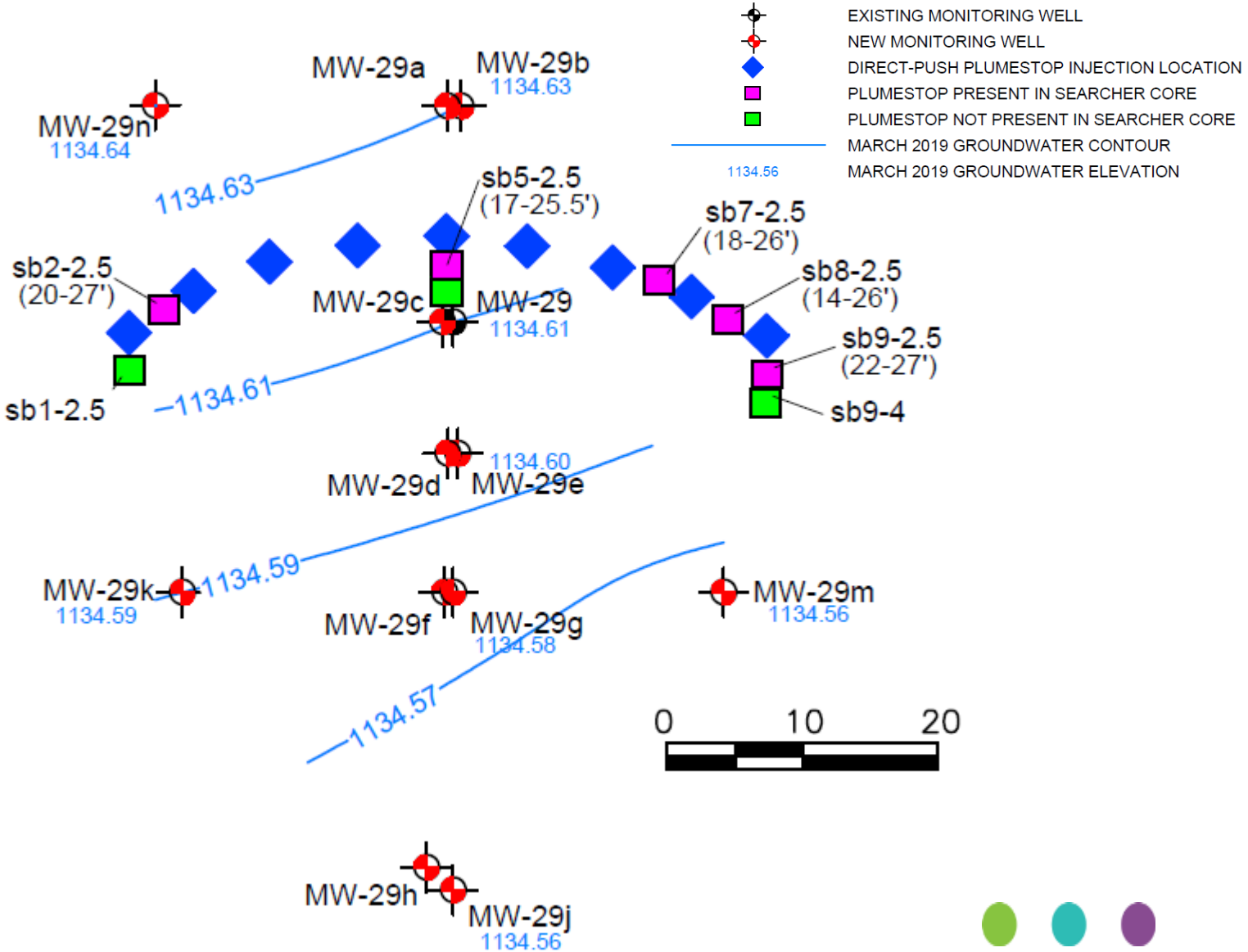
Camp Grayling Airfield – Conceptual Site Model

- Aquifer primarily Outwash/fluvial sand
- Coarsening down beds 1-2 feet thick
- Depth to water: 14-15 feet
- Depth to Clay: 27 feet
- f_{oc} ~ 0.02 – 0.04% (Walkley Black)
- Advective groundwater flow rate: ~2 feet per day (K~77-253 ft/day)
- Aquifer typically:
  - Aerobic (ORP: 25 – 200 mV)
  - Slightly basic (pH: 7-8)
  - Groundwater TOC ~ 1 mg/L
  - CEC ~ 9.5-11meq/100 grams soil (Ca^{+2}>>Mg^{+2}>K^{+1} or Na^{+1})



Camp Grayling Airfield – 2018 PlumeStop™ Injection Pilot

- Regenesis injected PlumeStop™ Oct. 1- 5, 2018
- Nine locations on 5-ft centers.
- 2400 lbs ea. of PlumeStop™ & PlumeStop Stout™ (8-10,000 mg/L; ~ 750-1000 gallons/pt)
- Bottom-up application (1-ft to 3-ft lifts; 14-26 ft bgs)
- Injection pressures/flow rates up to 90 psi & 8 GPM



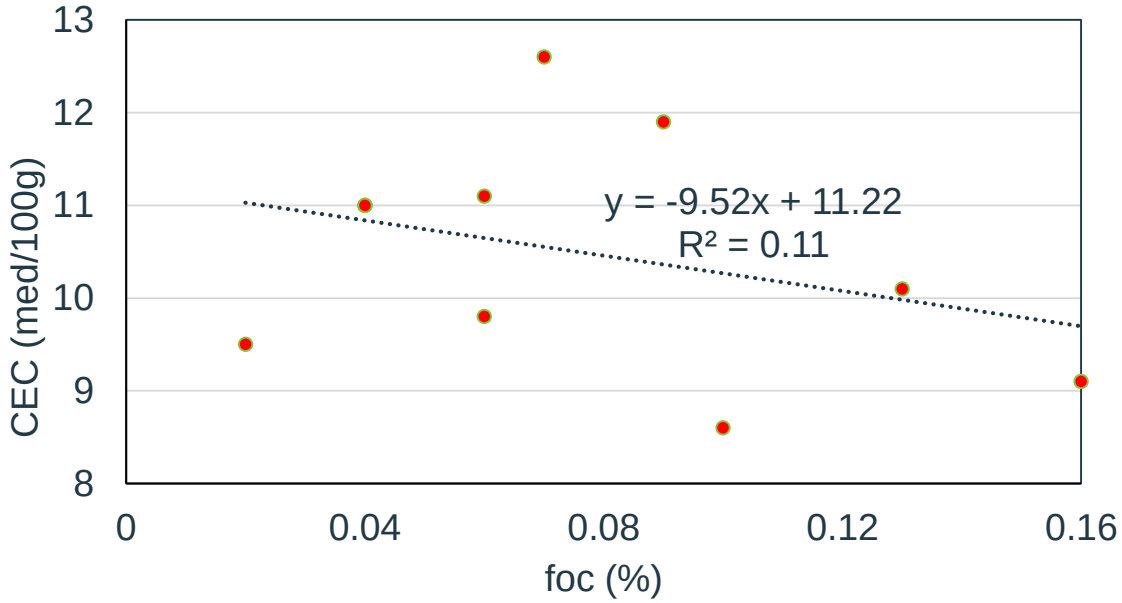
Camp Grayling Airfield – 2018 PlumeStop Injection Pilot

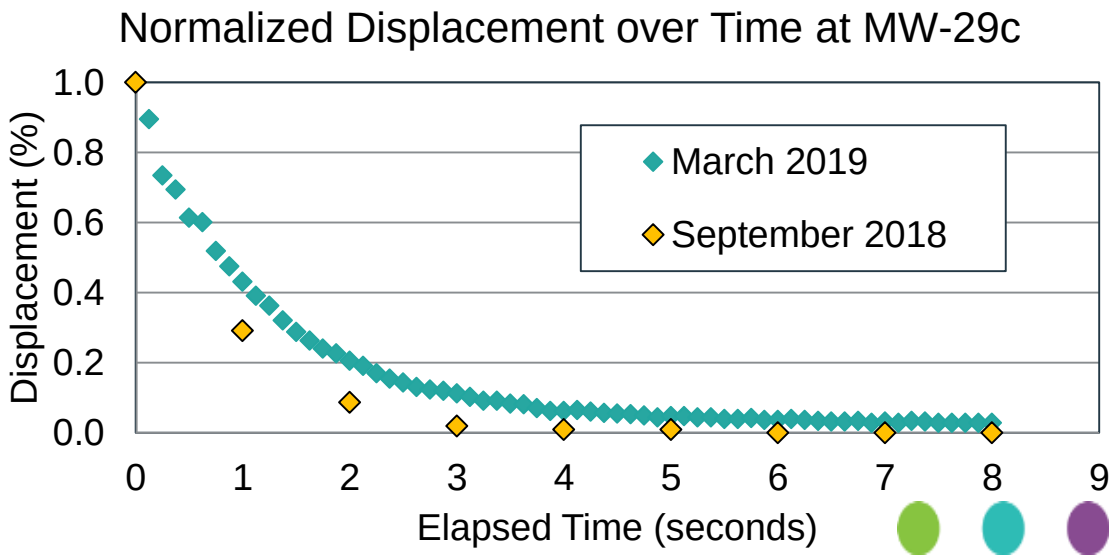
- Mixing Trailer
- Clean Water Supply
- Truck Mounted Geoprobe

1-2 µm Activated Carbon (Colloidal)

Camp Grayling Airfield – Soil Results

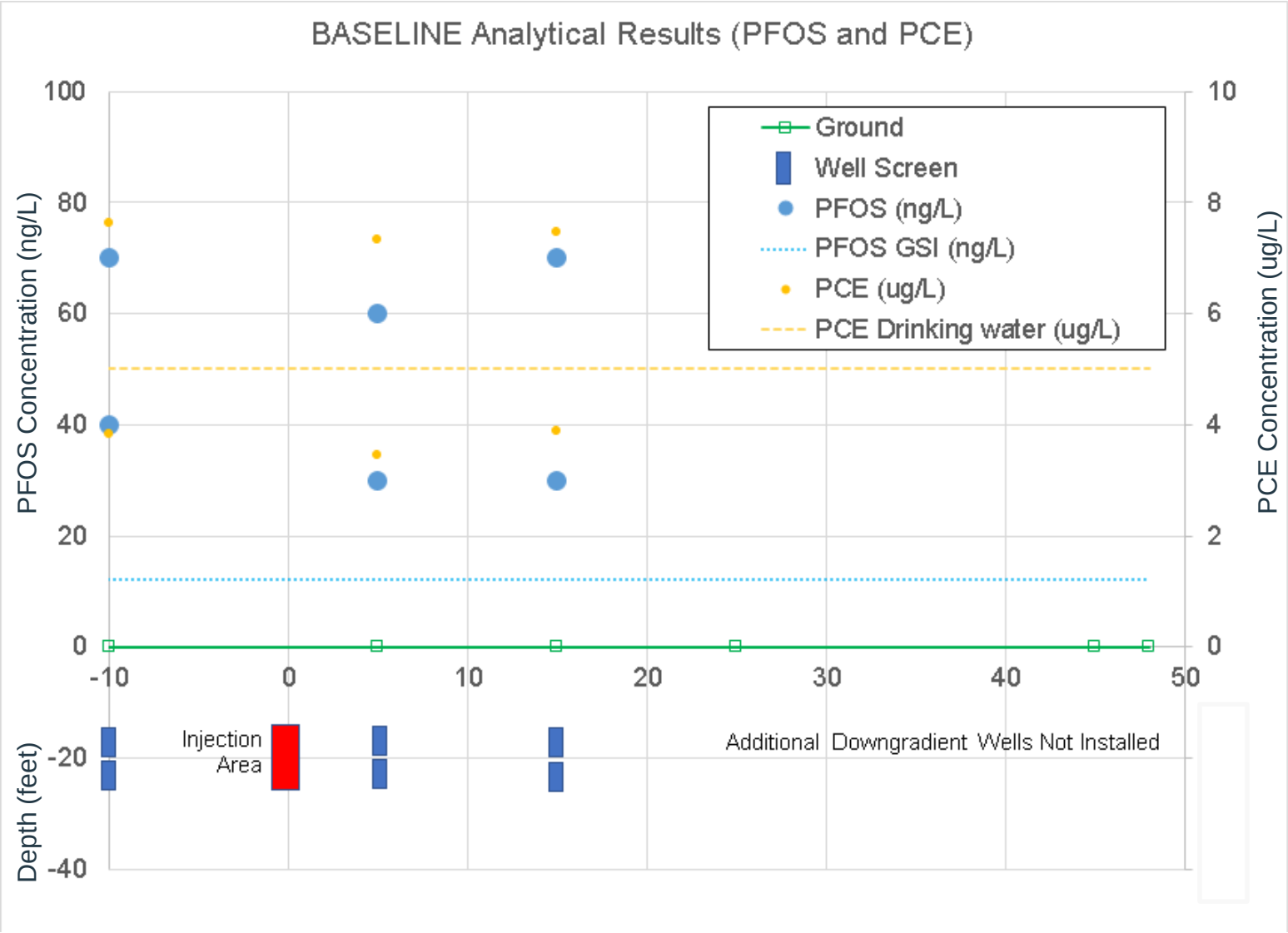
- Physical Testing:
- f_{oc} increased to 0.04% to 0.16% (including 0.09% where not visually observed).
- CEC ~ constant (8.6-12.6 meq/100g)
- No apparent correlation of CEC to f_{oc}
- Pre-/Post-Injection Slug Test Results Relatively Unchanged (Remains Fast!)





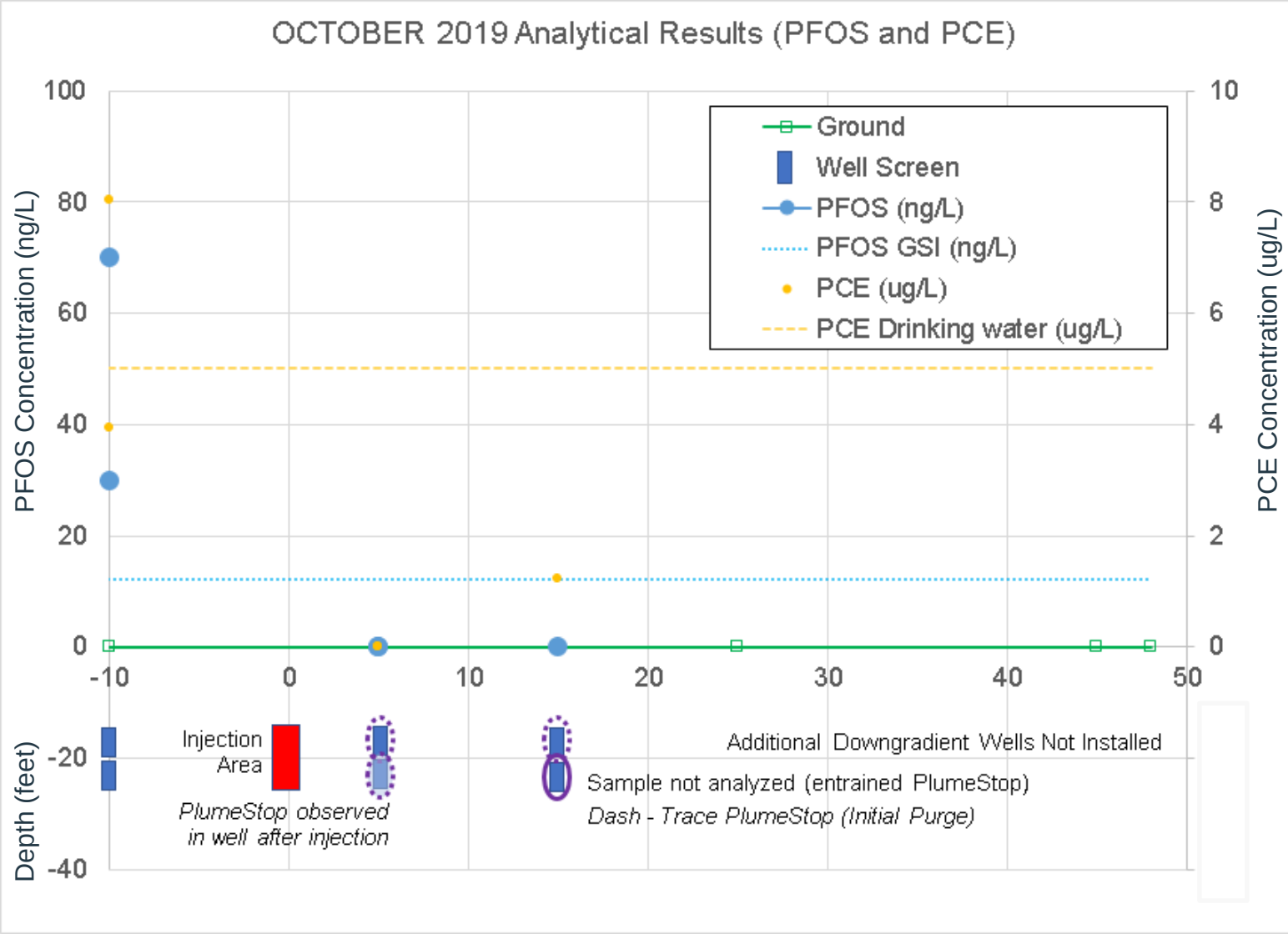
Camp Grayling Airfield – Time Series Results

- Baseline (shallow/deep)
  - PFOS =
    70 ng/L (water table)
    40 ng/L (deep)
  - PFHxS =
    60 ng/L (water table)
    50 ng/L (deep)
  - PFPeA = 10 ng/L (deep)
  - PCE =
    8.28 ug/L (water table)
    3.12 ug/L (deep)



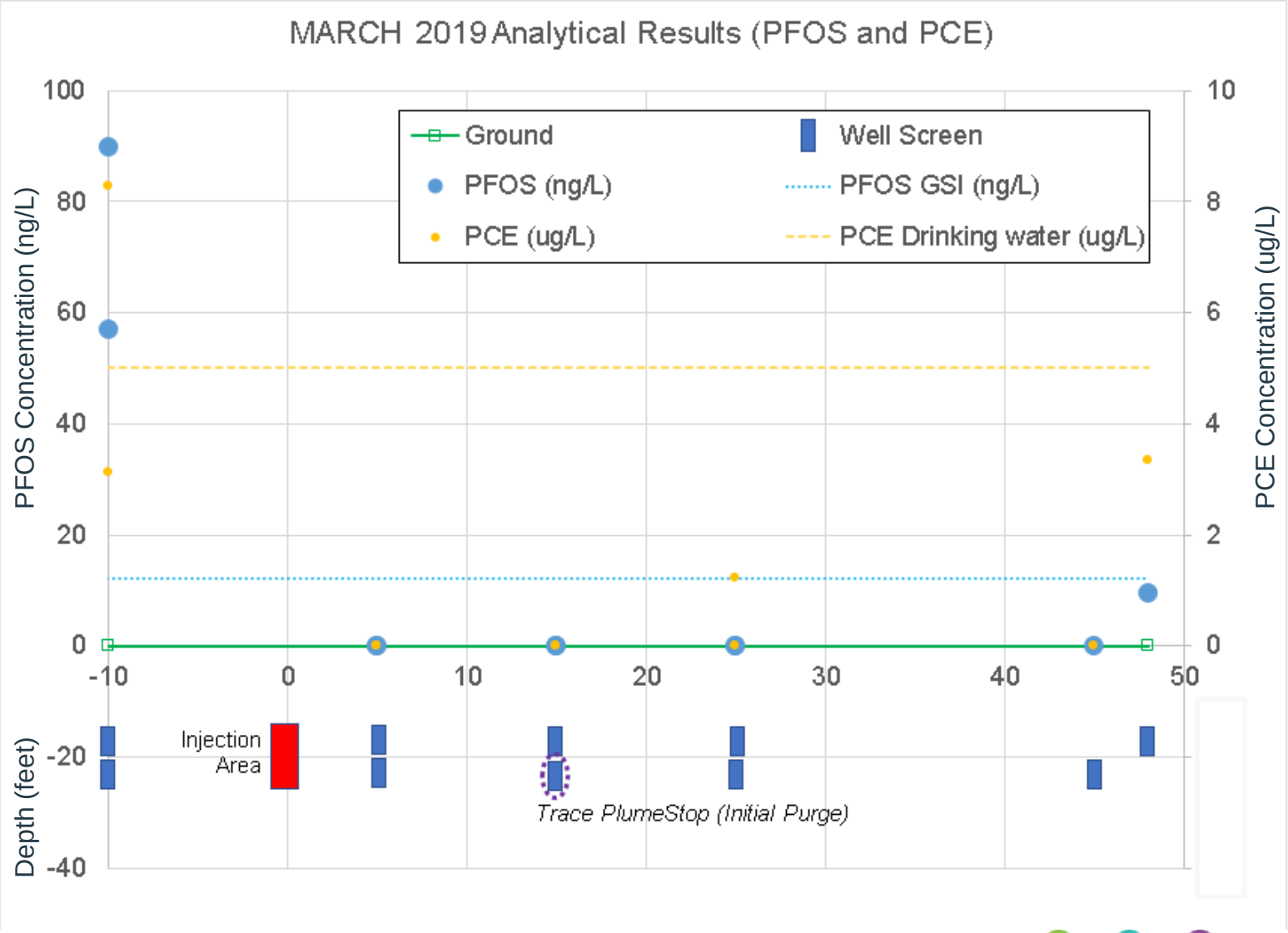
Camp Grayling Airfield – Time Series Results

- October 2018 (4 weeks)
  - No PFAS detected in water table or deep downgradient wells.
  - PCE =
    1.22 ug/L (water table only)
  - PlumeStop spreading
    ~ 15’ in downgradient water table well



Camp Grayling Airfield – Time Series Results

- ~ 6 months & 1 Year
  - PFOS =
    - 9.6 ng/L then ND (water table well; ~50 ft downgradient)
    - ND in all other downgradient wells
  - PCE
    - detected in shallow wells at 25 and 50 ft dg at 6 months
    - 2.0 ug/L (water table) and ND (deep) at furthest downgradient well at 1 year.
  - No PlumeStop “show” further downgradient



Carbon – Lessons Learned

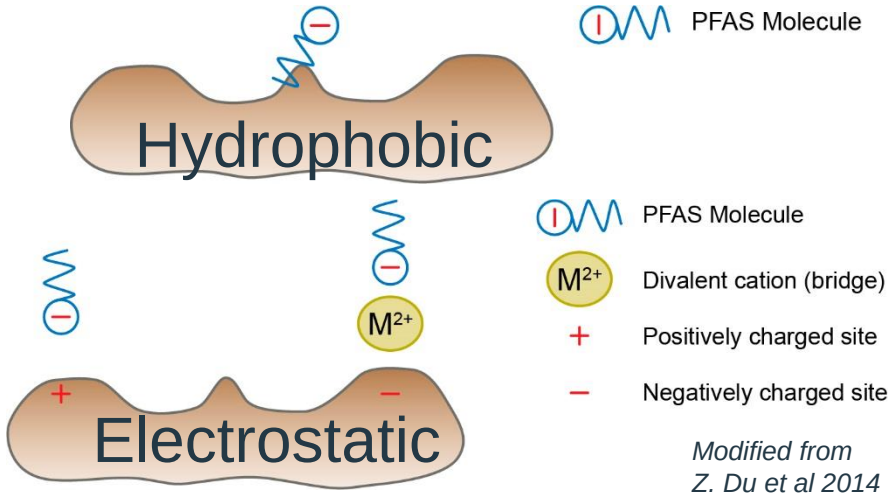
- Biochar and colloidal activated carbon effectively reduced PFAS in groundwater in each application.
- Heterogeneity in vertical distribution of carbon during injection occurs with both media – material follows (and treats) preferred migration pathways.
- Delivery of both media at the water table was a challenge.
- Baseline / Post injection slug tests were similar for both media - nominal impact on hydraulic conductivity when delivered via direct push methods.
- Baseline / Post injection slug tests in soil mixing area decreased by an order of magnitude but impacted groundwater appears to continue to flux through treatment cell.

Carbon – Lessons Learned

- Competition / kinetics can be predicted - Colloidal activated carbon sorbed low level PFOS in presence of PCE (and at higher efficiency), per Koc.
- Kinetics of short chain sorption?
  - Biochar – TCLP/groundwater show less reduction of short chains and carboxylic acids (e.g., PFBA and PFPeA).
  - Colloidal activated carbon - Low levels in treatment area; could not resolve potential competitive sorption rates for individual PFAS.
- Testing by SPLP and TCLP useful to assess retention/retardation.
- Longevity?
  - Leaching at 1-yr (Biochar ~1,5% loading rate) lower when compared to samples collected after mixing; PFOS result below 12 ng/L.
  - Both media show continued treatment at 1-yr mark

Carbon – Lessons Learned

- Sorption mechanisms may vary (media/Site) and complicate monitoring/assessment:
  - Colloidal activated carbon and Biochar enhanced TOC (hydrophobic tails)
  - Biochar also enhanced CEC – (electrostatic interactions).



Modified from Z. Du et al 2014

- Carbon impact on metals displacement/disassociation from soil matrix and/or carbon may extend beyond divalent cations.
- Metal-PFAS interactions in groundwater was a “local” effect.
- Importance/role of anions/soil anion exchange capacity has not been assessed in these studies.

Storm Water Anyone?