Implementing Effective *In-Situ* Permeable Colloidal Activated Carbon (CAC) Barriers to Stop Hydrocarbon Plume Migration

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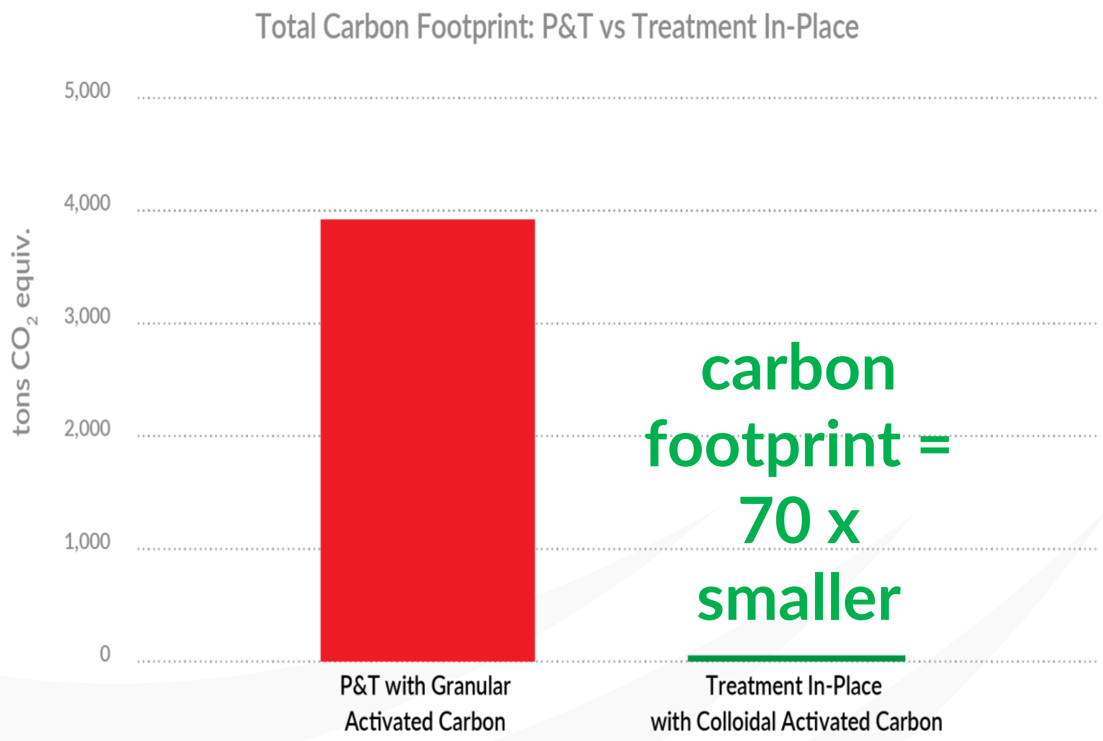
Social and Environmental Impact of CAC Barriers

- >95% reduction in greenhouse gas emissions vs P&T[1]
- Highly resilient (no electricity or moving parts)
- No contamination brought to surface
- Green – No O&M



1. Ramboll 2023 Sustainability-Case-study-PlumeStop-vs-PT-Final.pdf

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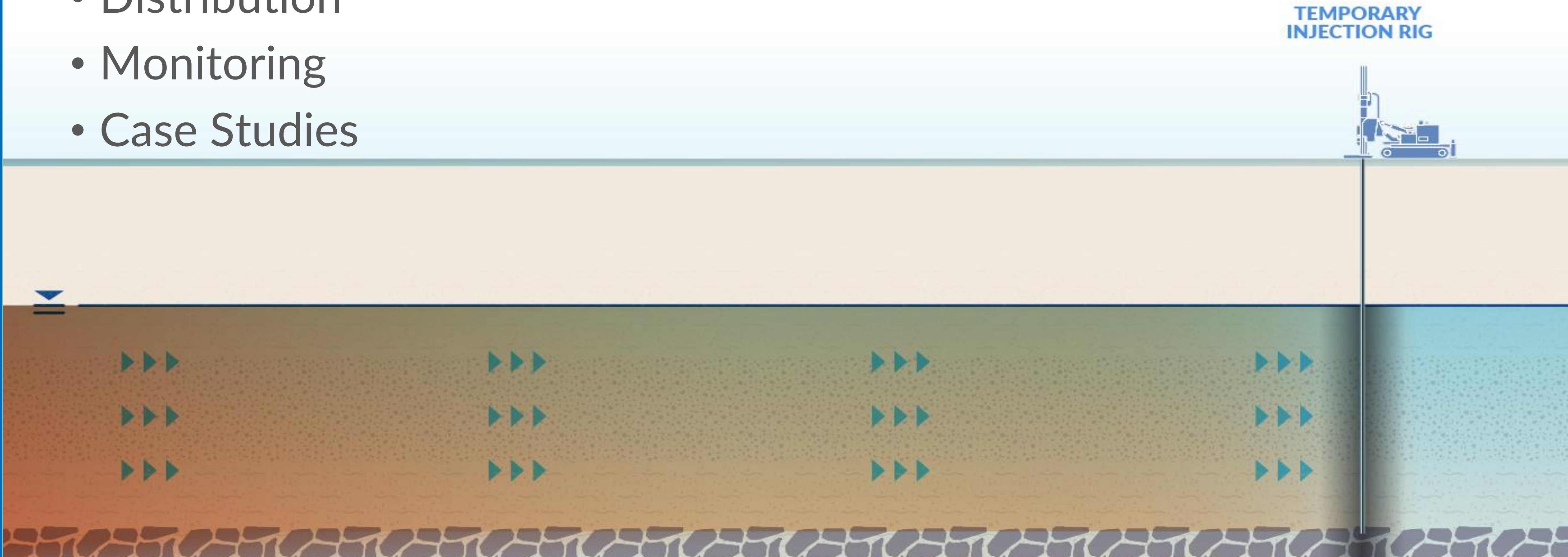
Design Considerations For Colloidal Barriers

- **Colloidal Advantages**
- Mass Flux
- Distribution
- Monitoring
- Case Studies



What Is A Colloid?

A colloid is a mixture in which particles of one substance are distributed evenly throughout another substance. Paints, milk, and fog are colloids.

CAC (left image) is a 1-2 micron activated carbon **colloid** dispersed in water.

A non-dispersed, non-colloidal activated carbon **solution** is shown on the right.

Stabilized Micro-Scale AC (Colloidal)

De-Stabilized Micro-Scale AC (Non-Colloidal)

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Does Colloidal Carbon Improve Distribution?

Colloidal Activated Carbon (CAC)

Carbon Type	Particle Size (mm)
Granular Activated Carbon	400-1,000
Powdered Activated Carbon	50-250
Micron-Scale Activated Carbon	1-2

CAC vs. PAC moving through the columns in 12 minutes

Powdered Activated Carbon (PAC)

Grain Size	Pore Throat Diameter (mm)
Medium Sand	8-50
Fine Sand	5-20
Silt	3-8

Colloidal activated carbon will move through soil and all other forms of non-colloidal carbon (CAC vs PAC) will not

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Field Distribution Research (Third Party)

Scientific Research Publishing

Journal of Water Resource and Protection, 2020, 12, 1001-1018
https://www.scirp.org/journal/jwarp
ISSN Online: 1945-3108
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Distribution of Colloidal and Powdered Activated Carbon for the *in Situ* Treatment of Groundwater

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Abstract

The use of *in situ* technologies for the treatment of groundwater containing various compounds of concern are widely accepted. These technologies include chemical reduction, chemical oxidation, anaerobic and aerobic bioremediation, and adsorption, among others. One requirement for the successful application of these technologies is the delivery of the remedial reagent(s) to the compounds of concern. A rapidly evolving *in situ* technology is the injection of adsorptive media such as activated carbon and ion-exchange resin including powdered or colloidal activated carbon. Activated carbon has a long-demonstrated history of effectiveness for the removal of various organic and inorganic compounds in above ground water treatment systems. However, due to constraints related to the particle size and physical properties of the activated carbon, the *in situ* application of activated carbon has been limited. Recent developments in the manufacturing of activated carbon have created a smaller particle size allowing activated carbon to be applied *in situ*. To evaluate if powdered and colloidal activated carbon can be effectively distributed in aquifers, the two types of carbon were injected using direct push technology adjacent to each other at four sites with varying geology. Evaluation of distribution was completed by sampling the aquifer prior to and post-injection for total organic carbon. The results of the studies indicated that both forms of activated carbon were effectively delivered to the targeted injection zones with both carbon types being detected at least seven meters away from the point of injection. The colloidal form of the activated carbon showed good distribution throughout the four targeted zones of injection with 93 percent of the samples collected having colloidal activated carbon present within them whereas the powdered activated carbon cells were more susceptible to aquifer heterogeneity with only 67 percent of the samples collected having activated carbon present. Preferential accumulation of activated carbon was

McGregor, R.(2020) Distribution of Colloidal and Powdered Activated Carbon for the in Situ Treatment of Groundwater. **Journal of Water Resource and Protection, 12, 1001-1018.**

CAC vs PAC Distribution Study

- **4 Sites:** 1 CAC and PAC per site (8 plots total)
- **Geology:** Fine sand, glacial till, glacial, fluvial deposit, find sand + silt
- **10m x 10m test cells, 3m spacing**

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Field Distribution Research

Method

- 520 soil samples taken from soil cores (~65 per cell)
- Measure for total organic carbon (TOC) to determine presence of AC

Horizontal Detections

- **CAC** - detected in 94.4% of samples
- **PAC** - detected in 42.4% of samples

Vertical Detections

- **CAC** - homogeneous distribution
- **PAC** - thin fracture distribution

McGregor, R.(2020) Distribution of Colloidal and Powdered Activated Carbon for the in Situ Treatment of Groundwater. Journal of Water Resource and Protection, 12, 1001-1018.

Horizontal Detection

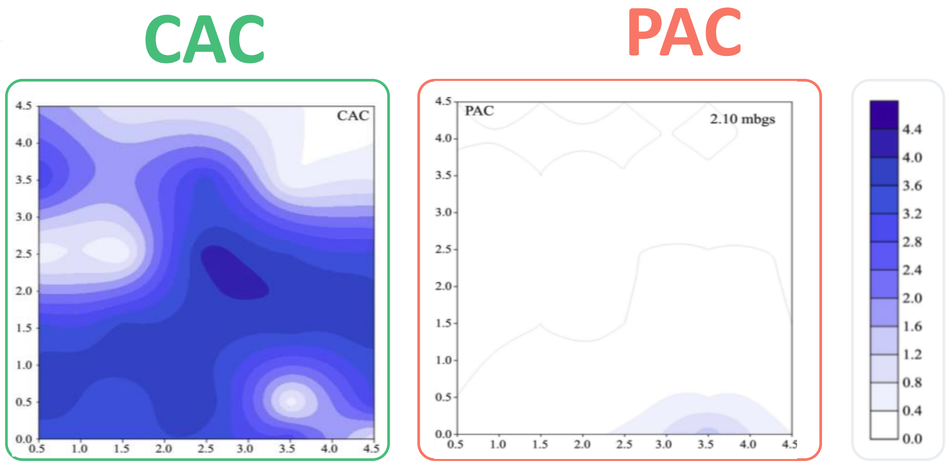
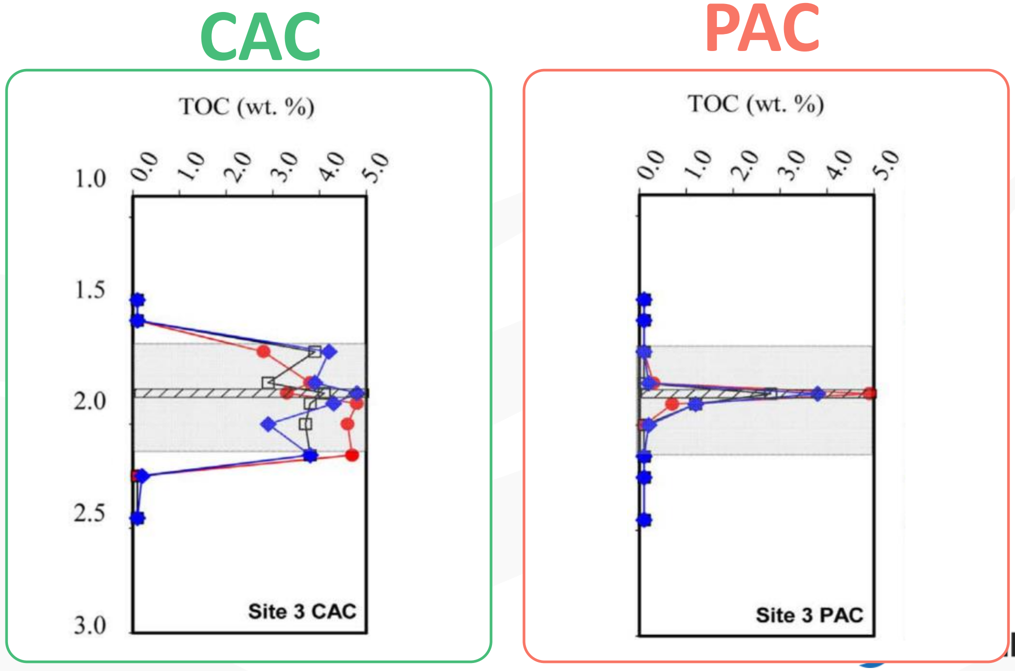


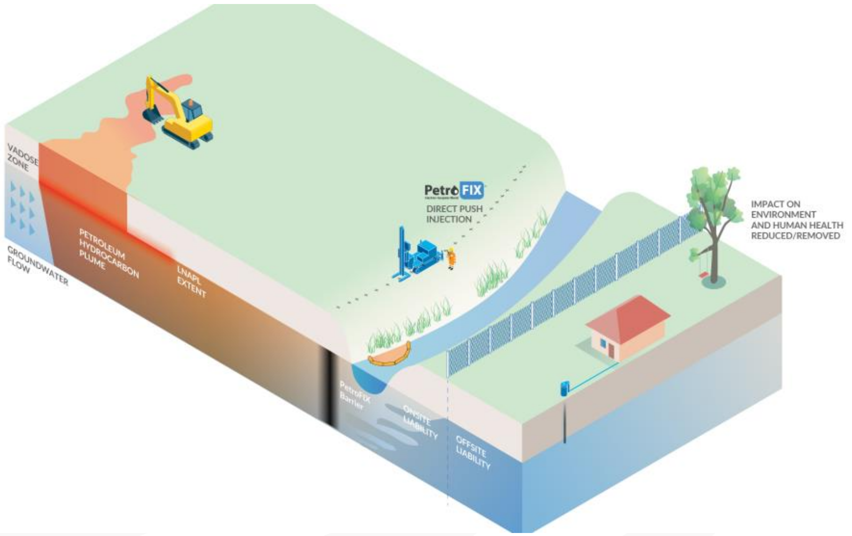
Figure 5. Total organic carbon (TOC) plots for the PAC and CAC test cells at Site 3 following the injection of the CAC and PAC at various depths (1.70, 1.85 and 2.10 mbgs).

Vertical Detection



Benefits of In Situ Permeable Reactive Barriers (PRBs)

- Contain plume during source remediation
- Reduce treatment scope (reduced grid size)
- Reduce mass discharge to accelerate natural attenuation
- Applicable to a wide range of contaminants
- Green – no O&M, low footprint



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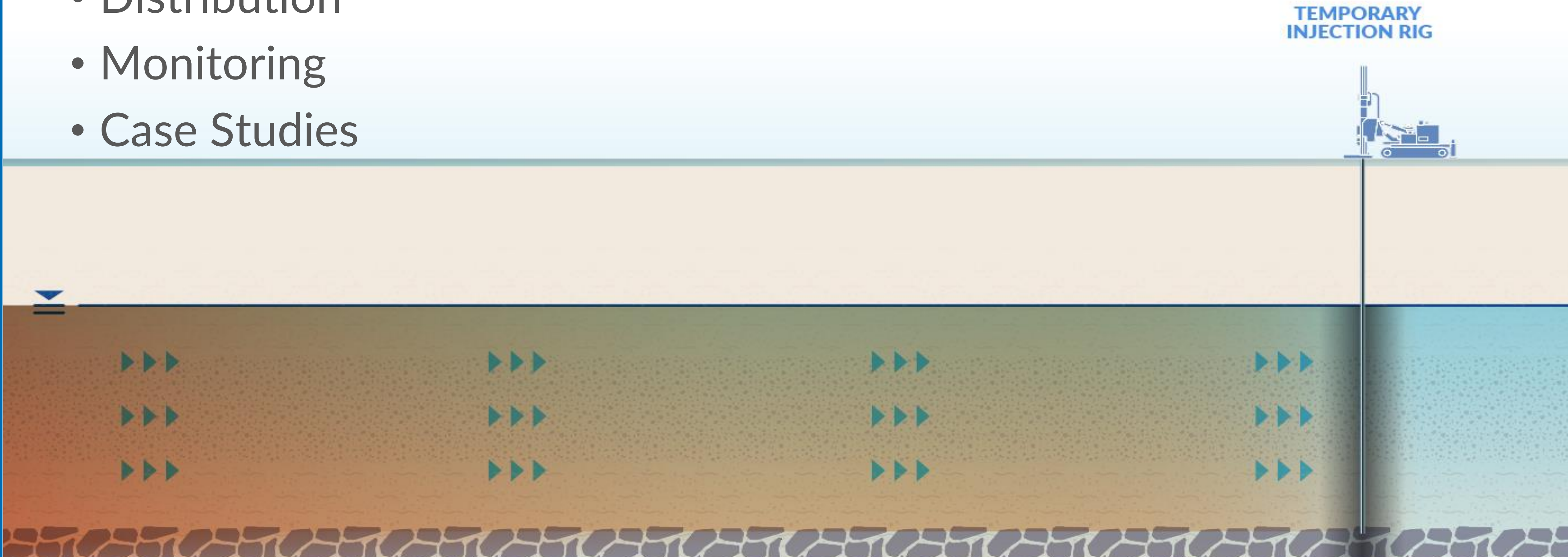
Design Considerations For Colloidal Barriers

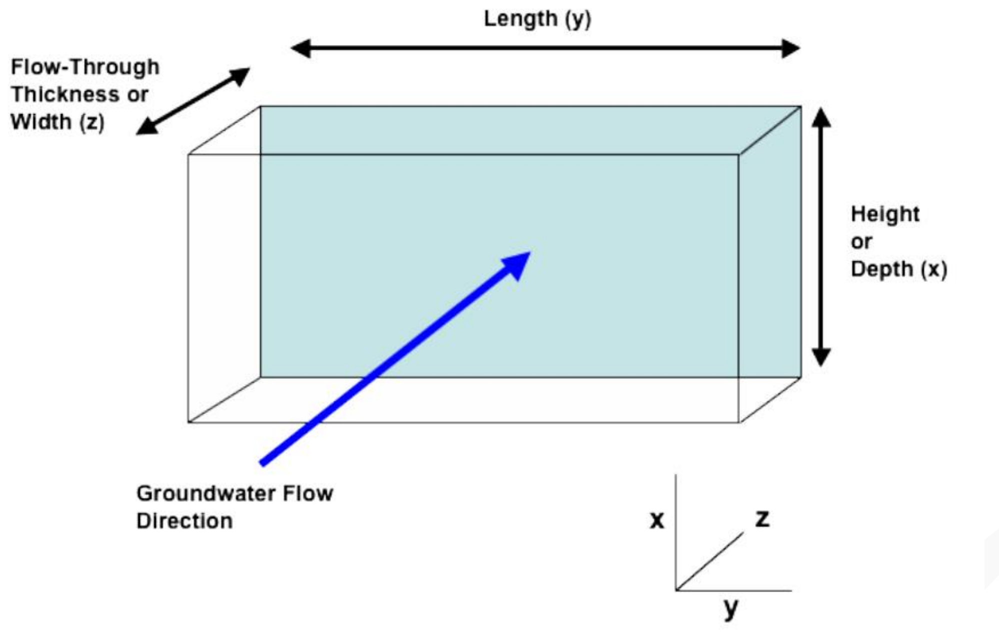
- Colloidal Advantages
- **Mass Flux**
- Distribution
- Monitoring
- Case Studies



Design and Construction of Colloidal iPRBs

A competent barrier requires:

- Good remedial conceptual model
- Appropriate reactive reagent
- Gapless placement of reagent
- Proper reagent dose and dimension



Idealized Barrier Cross Section and Average Mass Flux

Source: ITRC

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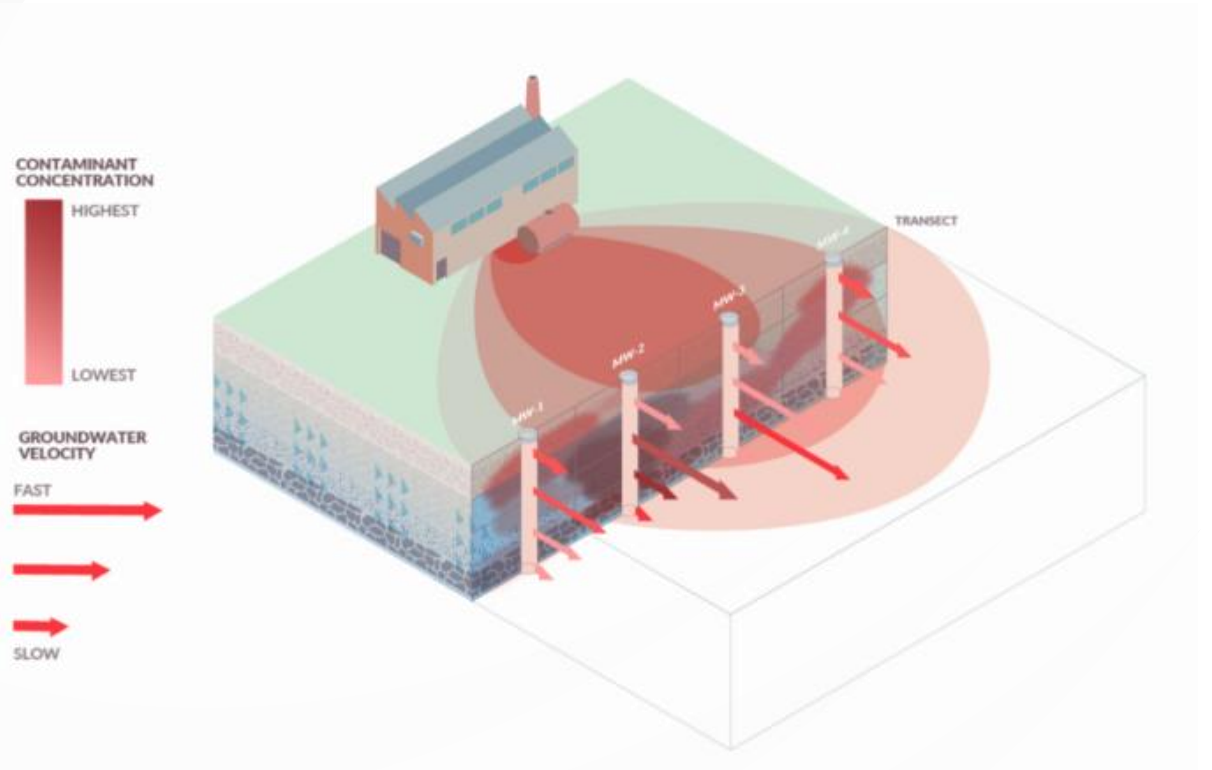
Design and Construction of Colloidal iPRBs

Mass Flux = Contaminant mass moving across a unit area (aquifer) perpendicular to the groundwater flow direction (mg/m/day)

Determines:

- Spacing, dose, number of points, number of rows
- Allows for strategic, accurate loading rates

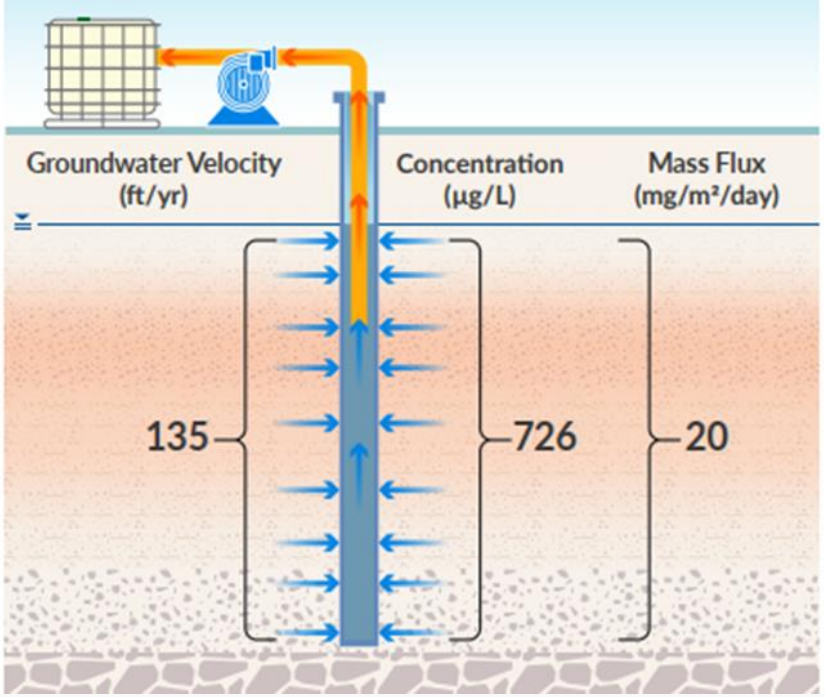


Actual Barrier Cross Section and Variable Mass Flux

Why is Mass Flux Important For Barriers?

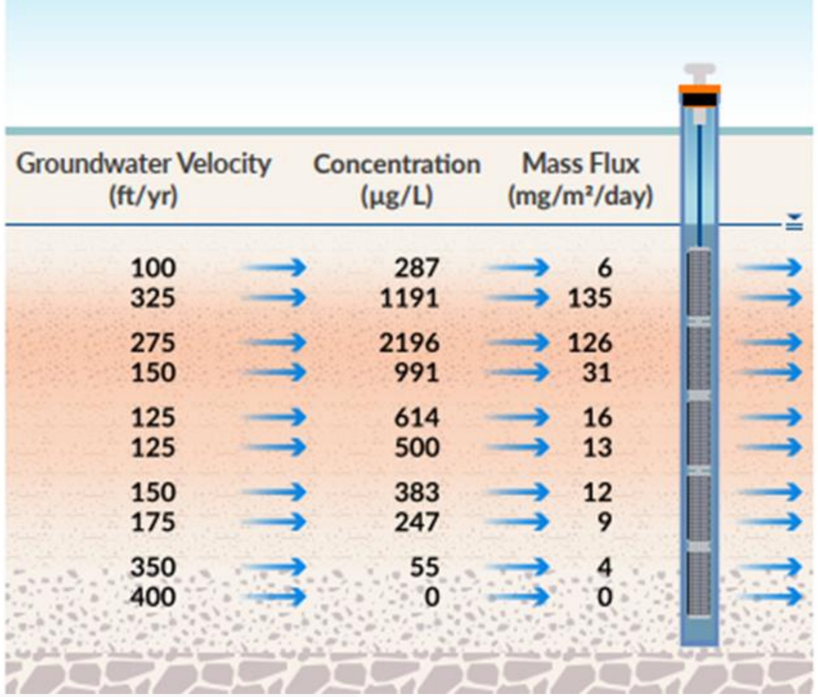
Bulk Average Methods (Pump/Slug Test)

- Does NOT delineate velocity and mass flux
- No data resolution
- Not ideal for in-situ remediation designs



Higher Resolution Methods (FluxTracer)

- Identifies zones with highest flux
- Optimize product placement
- More accurate insight into PRB longevity



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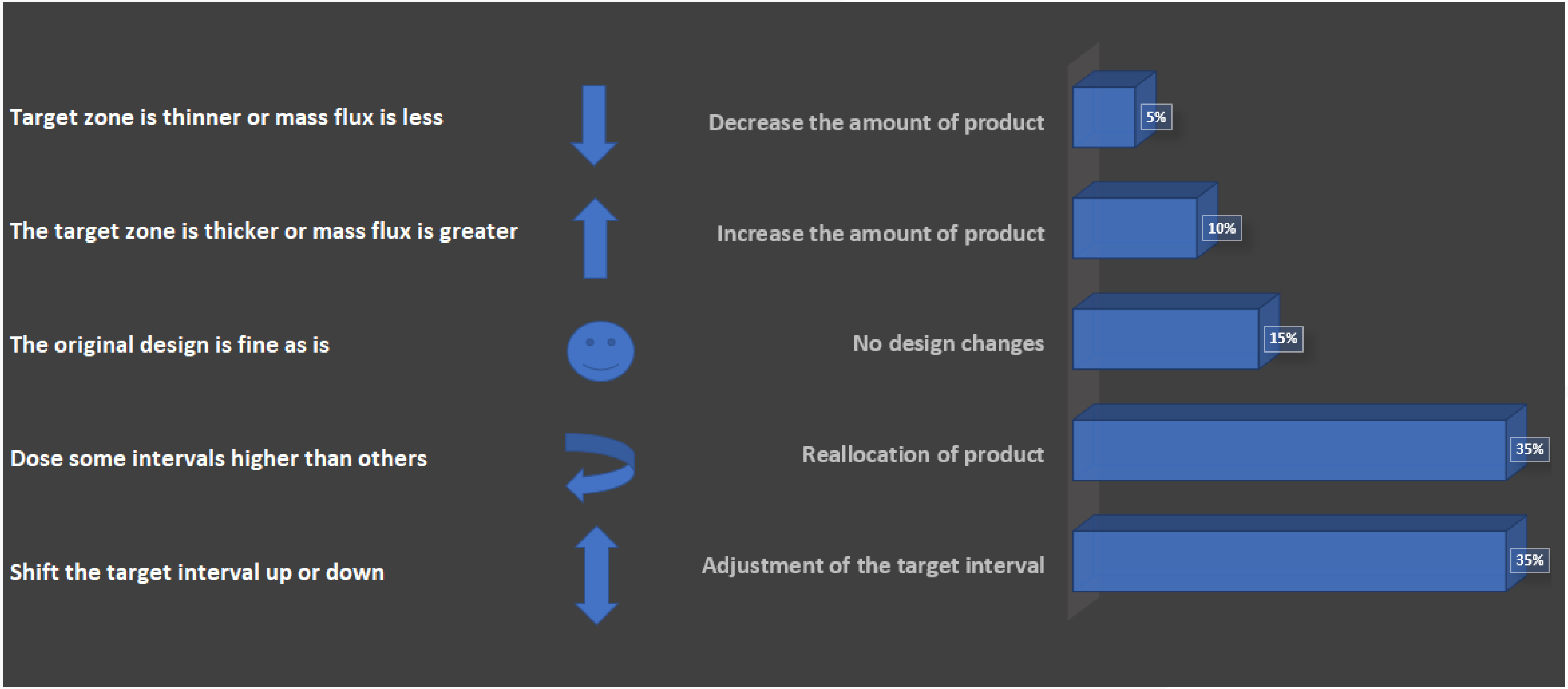
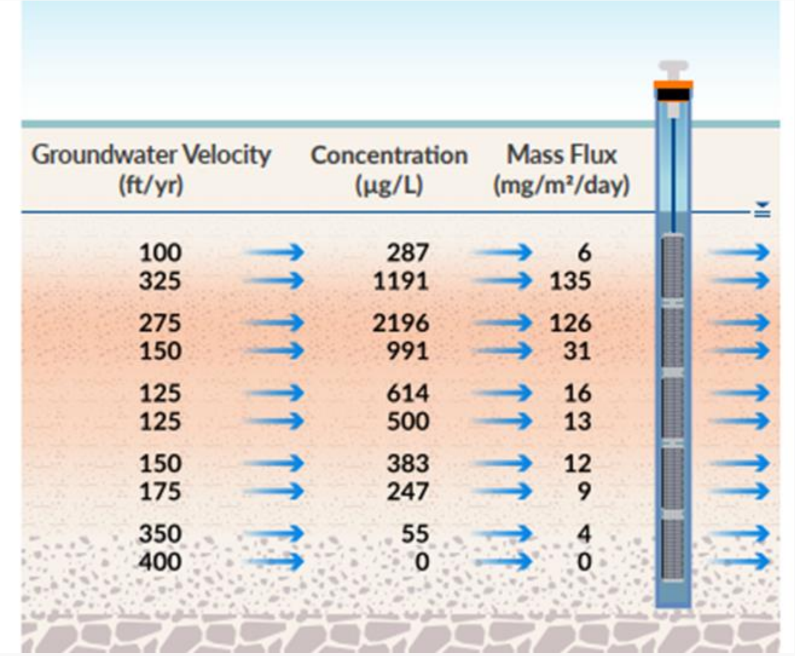
How Flux Data Informs on Remedial Designs



Measuring Mass Flux?



90% of the mass may be flowing through as little as 10% of the screened interval

EnviroFlux™ Passive Flux Meter *(www.enviroflux.com)*

Scan QR code for Mass Flux Webinar (not EnviroFlux related)

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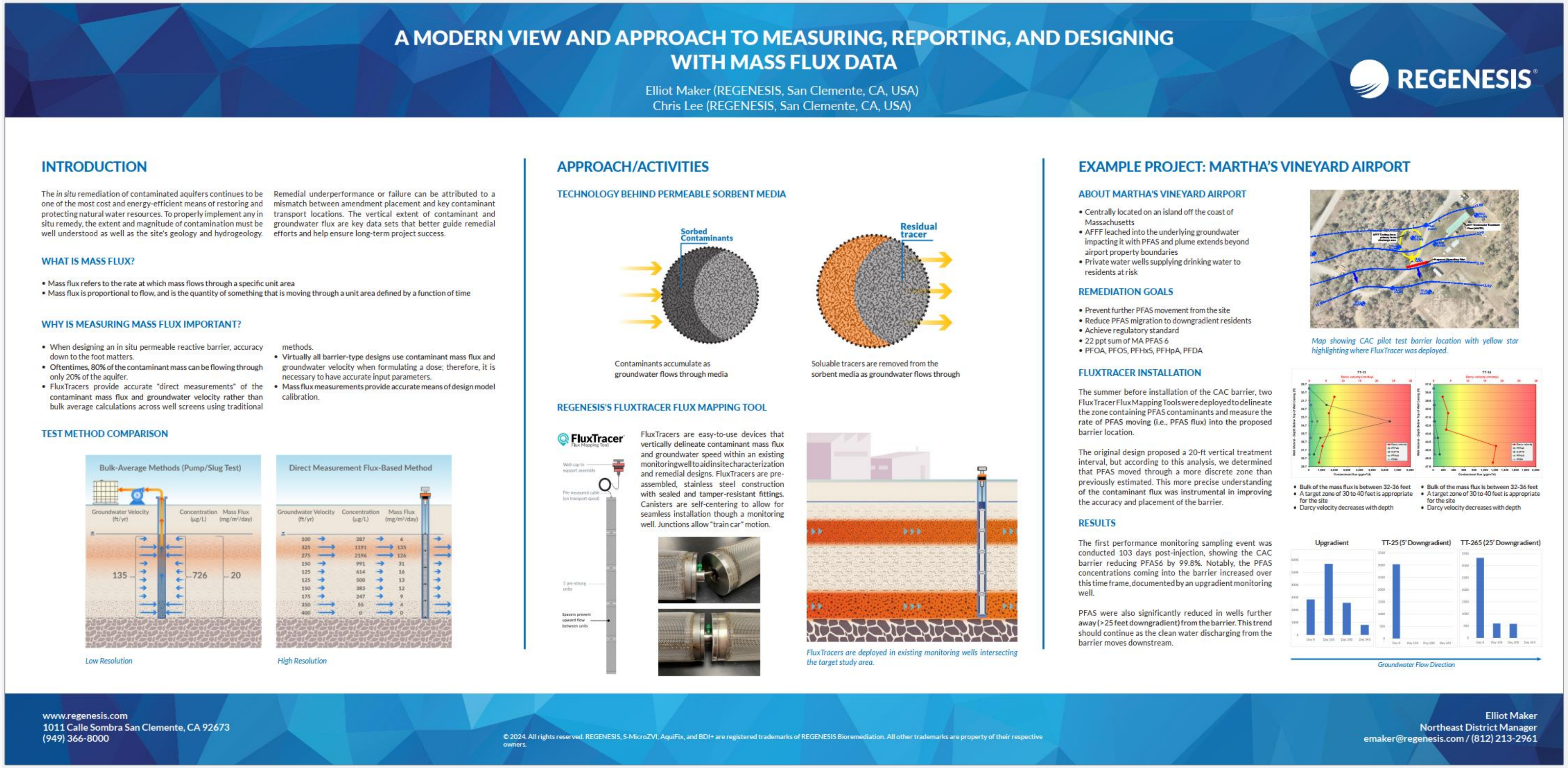
Wednesday Poster Session

A Modern View and Approach to Measuring, Reporting, and Designing With Mass Flux Data



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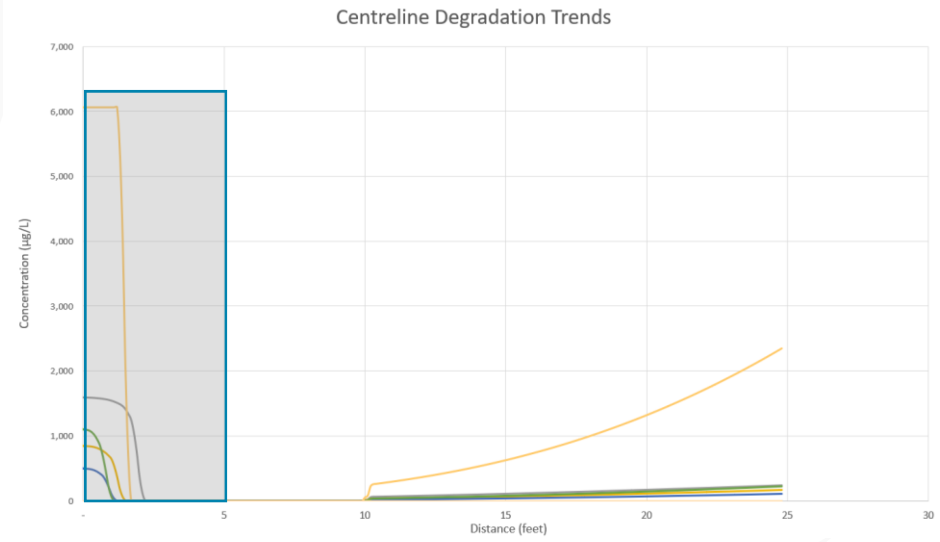
In Situ Remediation

Designing the Treatment

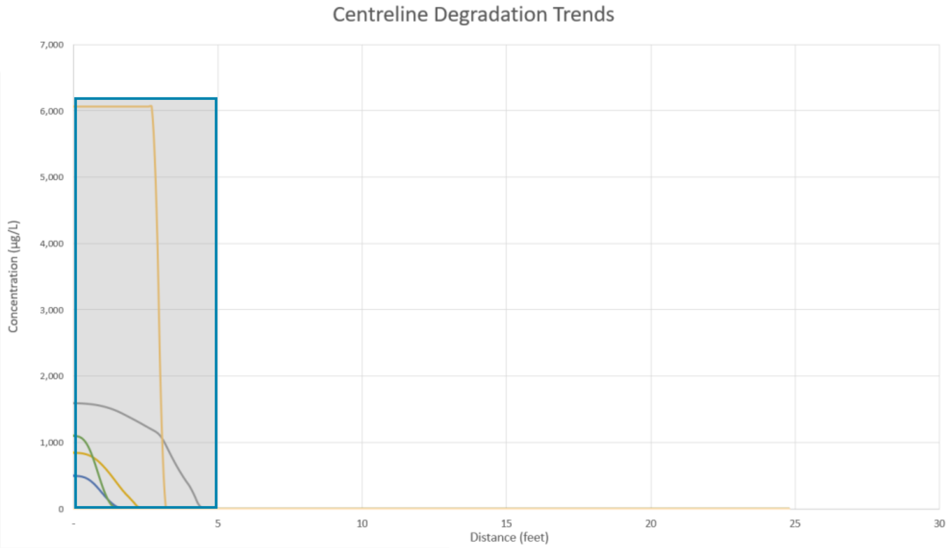
Barrier lifespan modeled on isotherms, dynamic sorption

Dose based on:

- Contaminant flux
- 1st Order Bio Rates
- Dimensions (length, width)
- Competitive Sorption
- Back Diffusion
- Time



1 Year



5 Year

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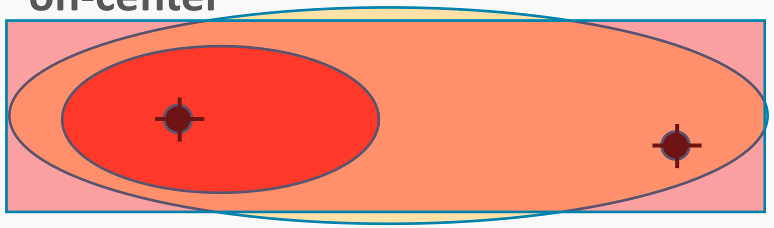
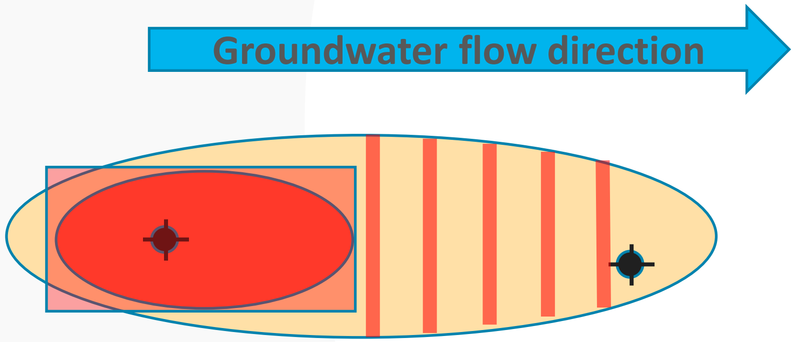
Optimization With Strategic Barriers

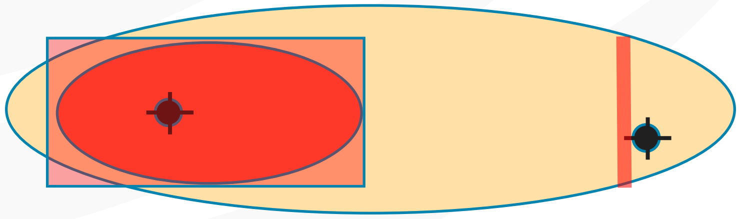
20,000 SF Plume, Grid Spacing 6.5’-on-center



470 injection points; 105,000 gallons water, 35 days in field



300 injection points; 65,000 gallons water
22 days in field



200 injection points; 50,000 gallons water
17 days in field

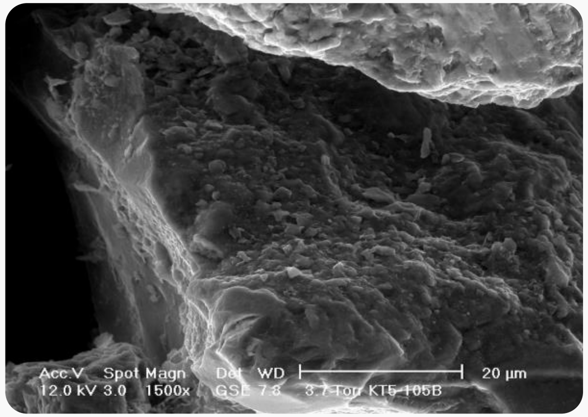
Monitoring well

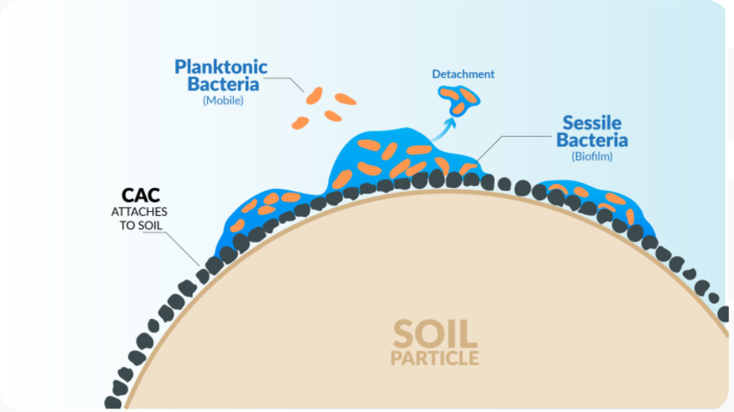
Injection grid

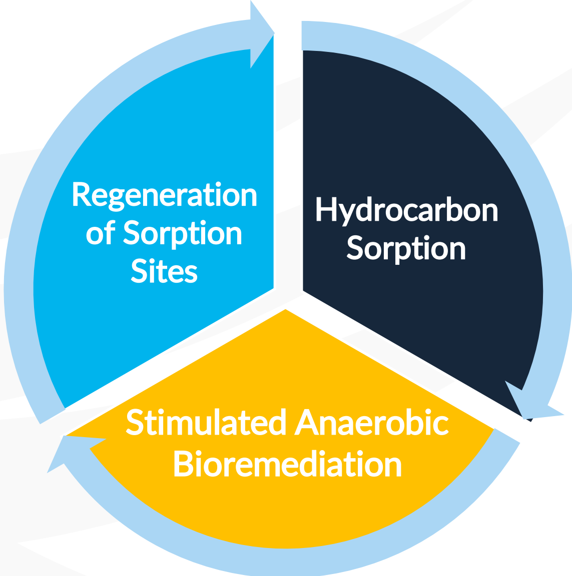
Does PetroFix Increase Longevity?

PetroFix Remediation Fluid

- PetroFix coats soils in flux zones with a micrometer-thick layer – contaminants adsorb
- Contaminant flux from advection or back-diffusion captured
- **NO_3 + SO_4 kick-start bioremediation = biofilm formation**
- ***YES*** - *In situ* carbon regeneration = contaminant destruction and multi-year longevity







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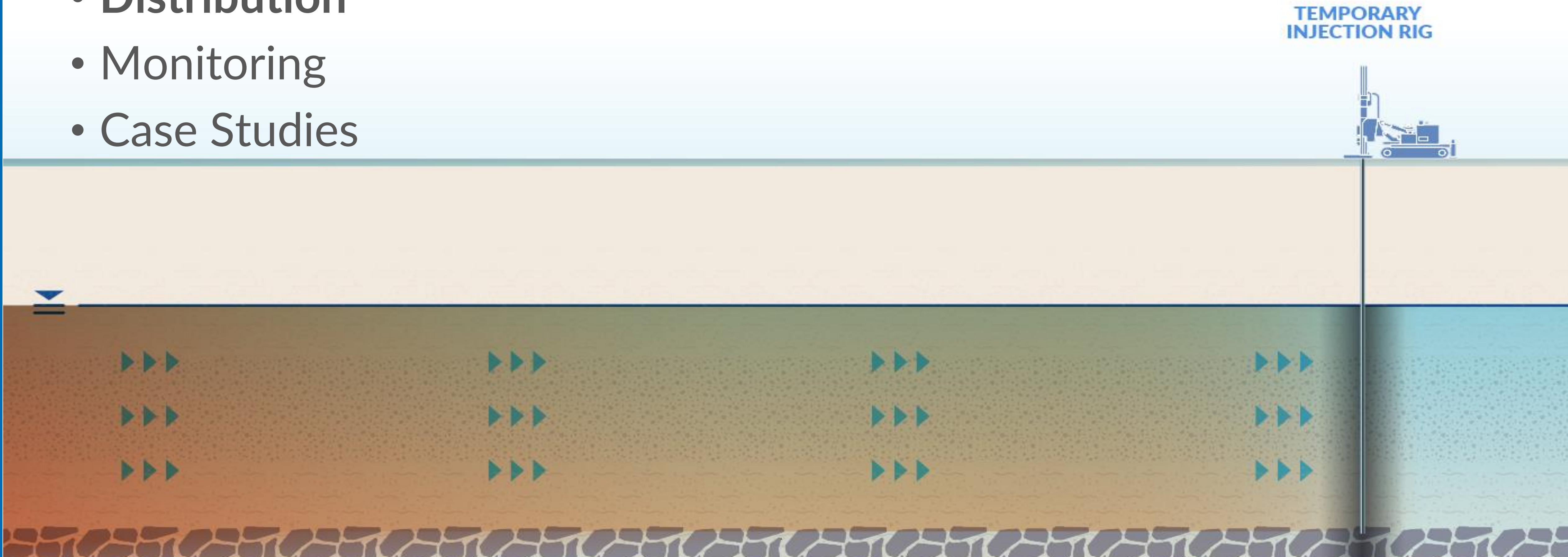
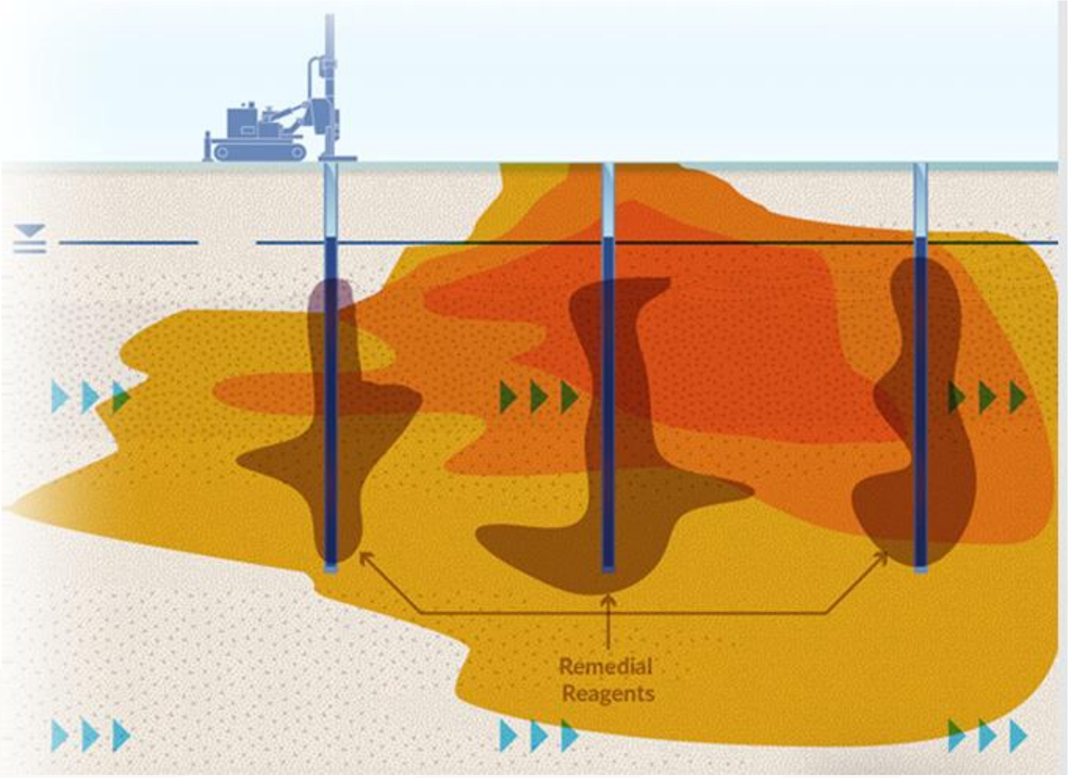


Construction

Distribution and Contact

Poor remediation amendment distribution is a principal limiting factor of performance for in situ remediation[1]

Monitoring of injection subsurface conditions should inform real-time adaptation of the delivery approach[2]



1. Battelle/NAVFAC, 2013 – Injection and Distribution of Amendments
2. ITRC, 2020 – Optimizing Injection Strategies

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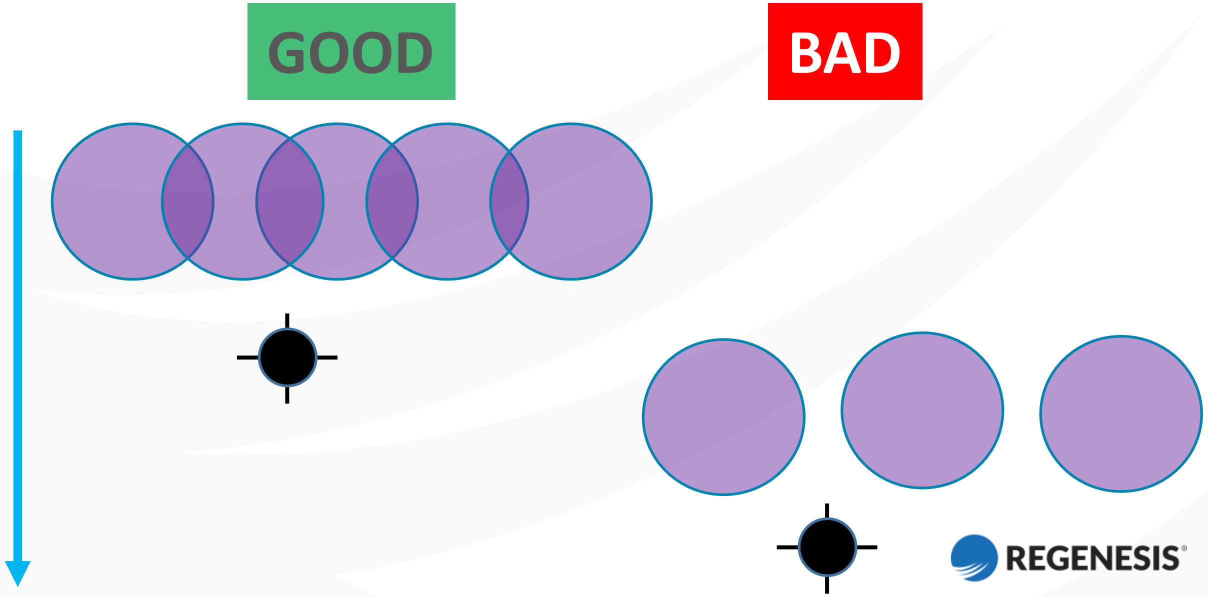
Distribution Verification?

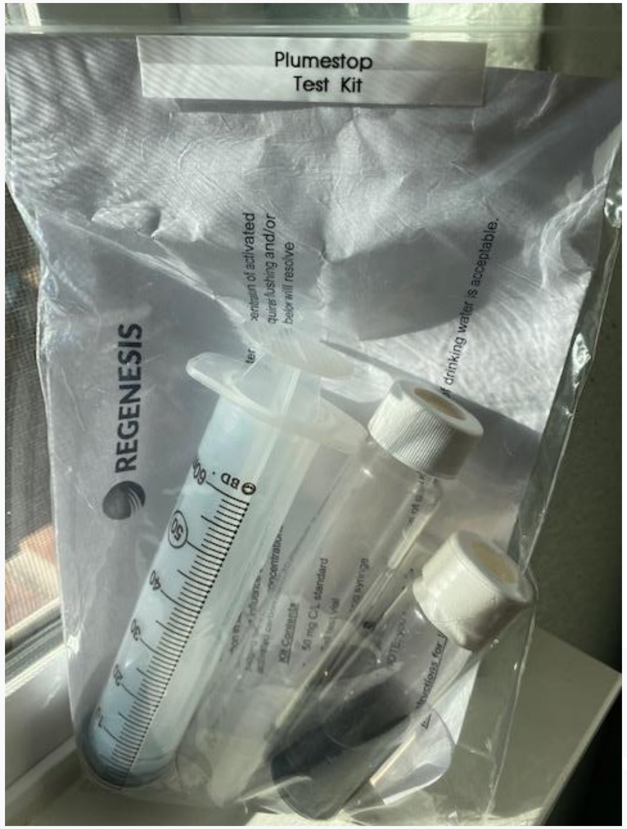
- Don’t let economic pressure necessarily dictate spacing for you
- Field test if you feel differently

SOIL TYPE	DIRECT PUSH INJECTION POINT SPACING (feet on center)	MINIMUM EPVF %*
COARSE >75% SAND/GRAVEL	6.5	60%
FINE >75% SILT/CLAY	5.0	40%
MIX OF COARSE AND FINE	6.0	50%
BEDROCK	6.0	40%

** EPVF % = Effective Pore Volume Fill Percentage*



CAC-Distribution Confirmation



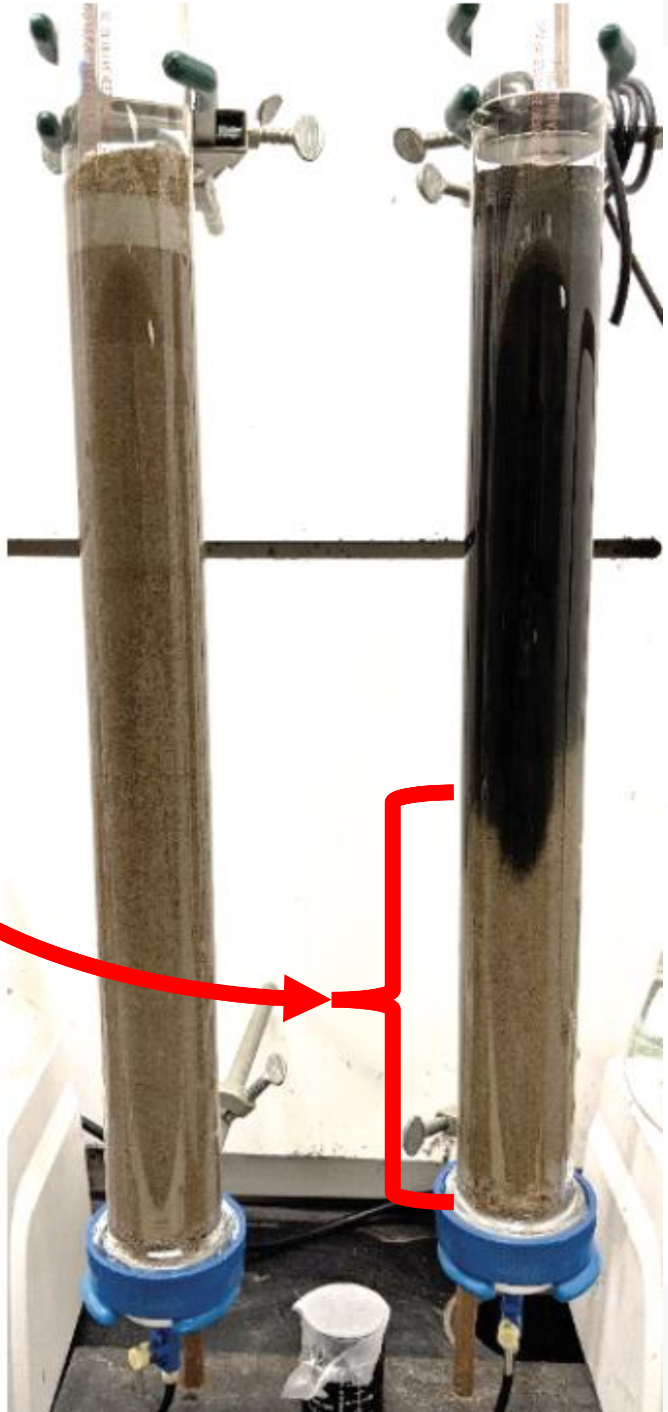
Does CAC Stop Moving or Does it Wash Out?

Right column: CAC solution applied and fed tap water for 24 hours.

NO CAC elution from the column

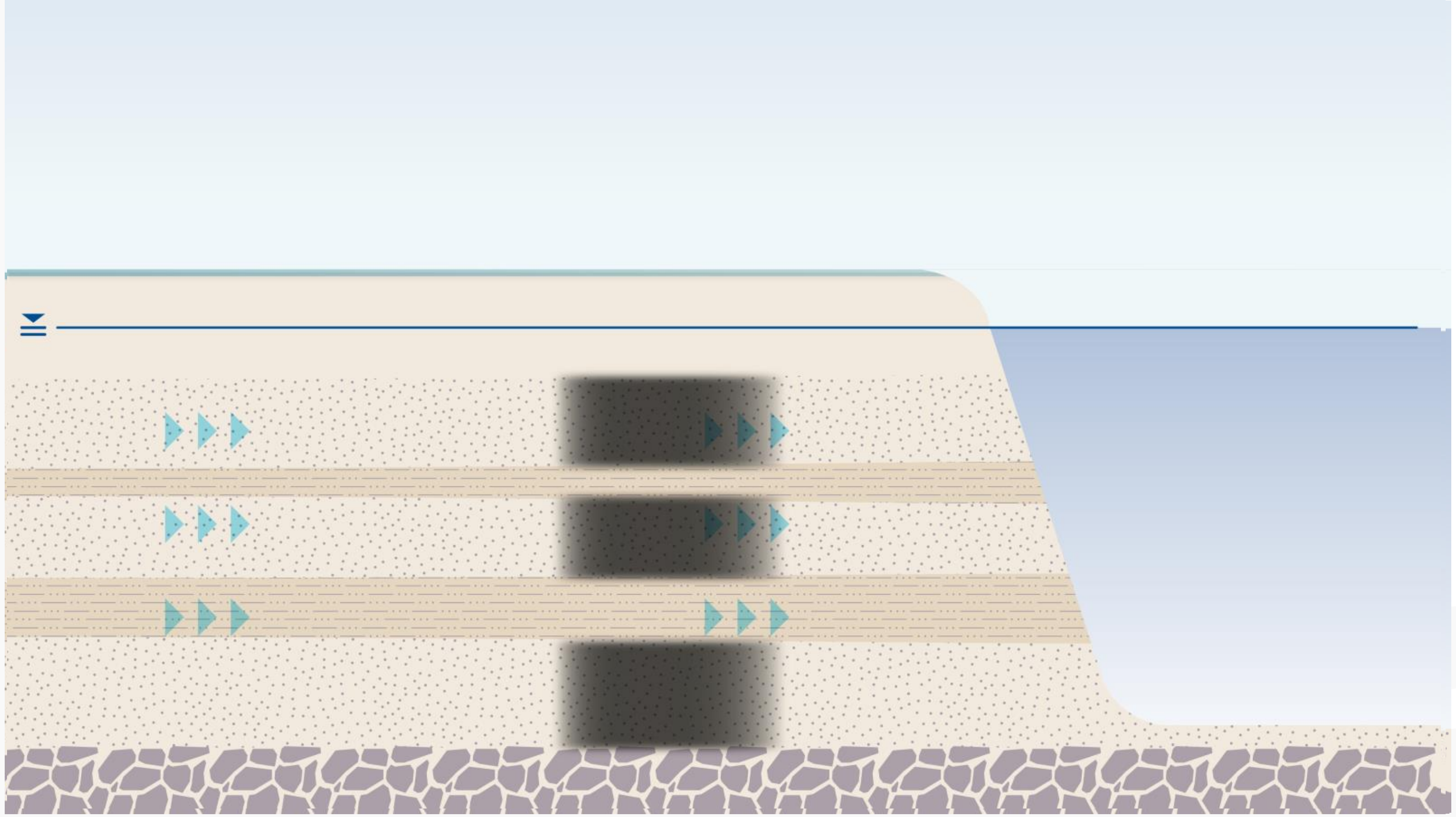
Higher surface area correlates to faster attachment

Post application movement is minor



The control (left) and CAC-treated (right) columns used in the study to demonstrate the ability of CAC to capture small diesel spills.

CAC Can Be Park if Needed

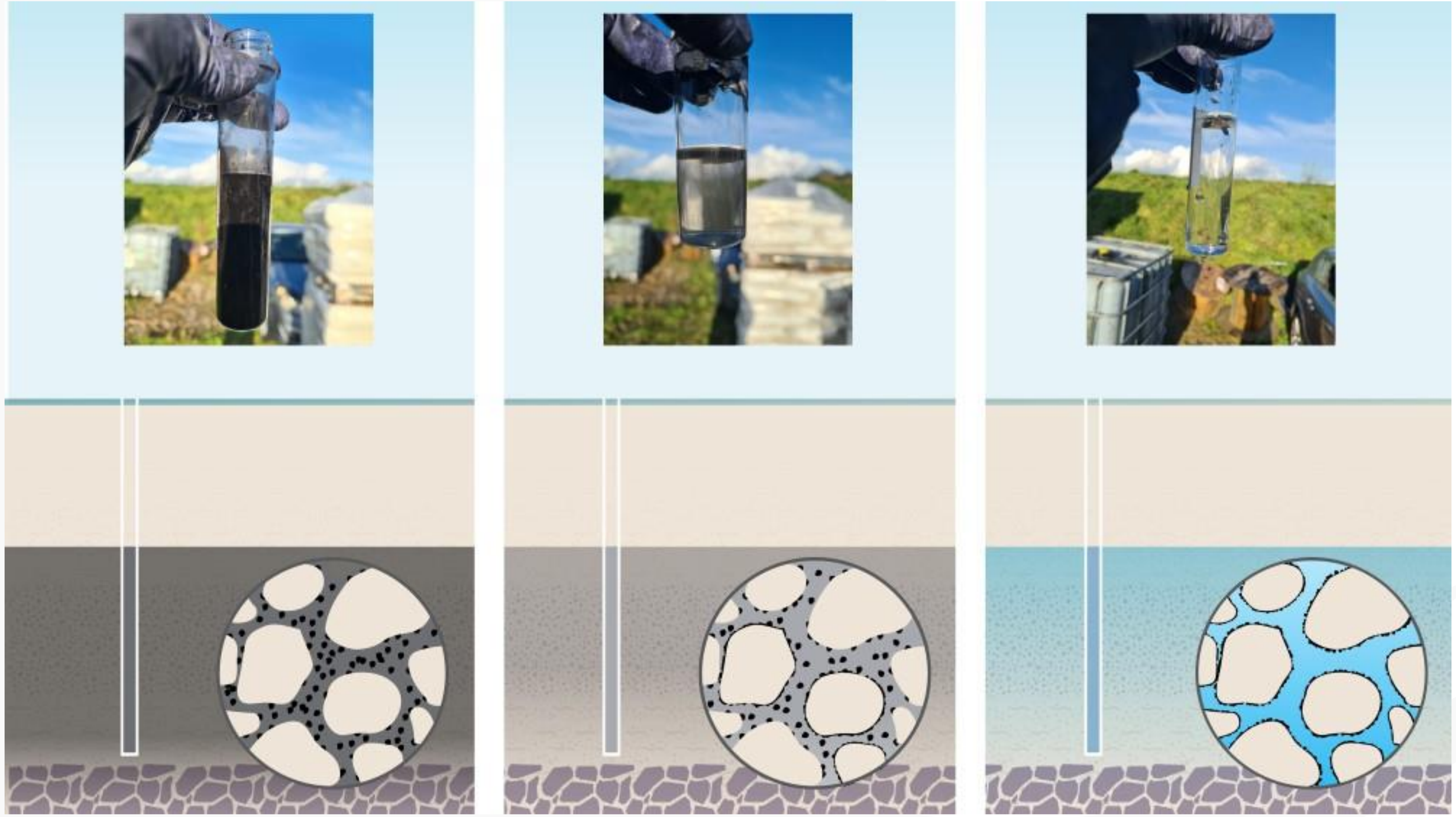


- CAC usually adsorbs to soil before moving out of the injection area
- <0.5% of injection mass to turn water very black

Option:

For High flow and/or low surface area (i.e. gravel/coarse sand) “Parking” is a solution

What Is Exactly "Parking"?



Applying Chemistry To Break the Colloidal Nature of CAC and Accelerate Flocculation

Di-Valent Cationic Salts such as Calcium Chloride ($CaCl_2$)

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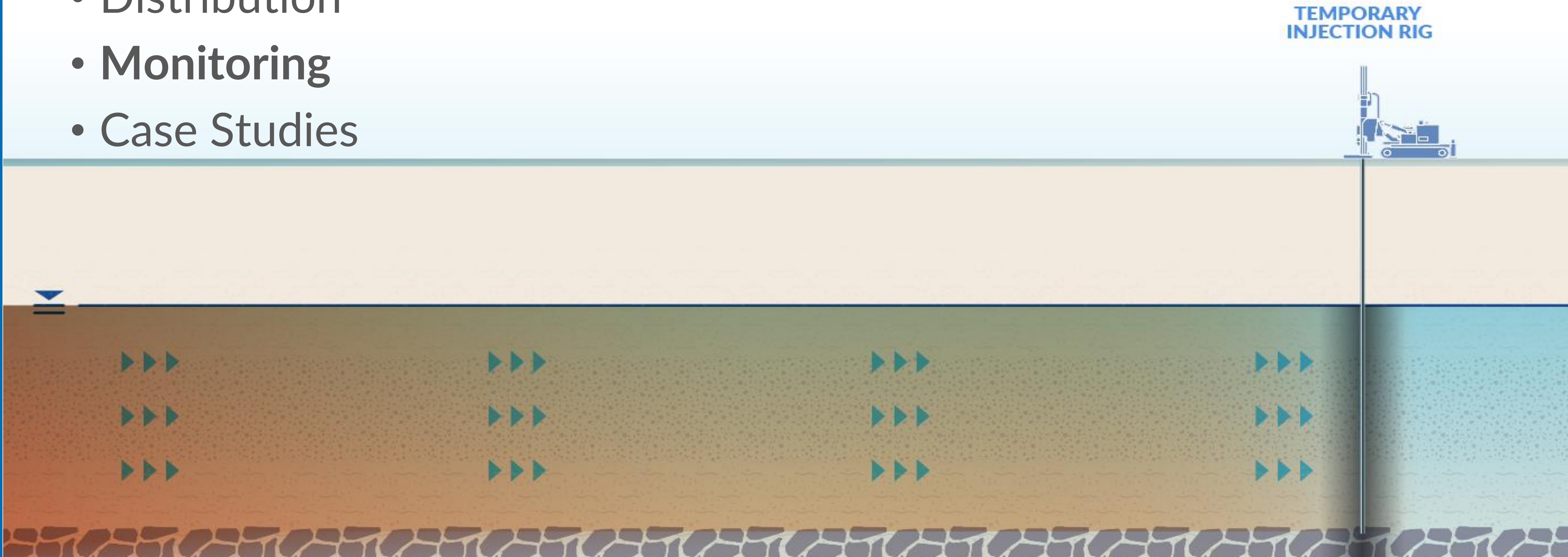
- Distribution
- **Monitoring**
- Case Studies



Injection Monitoring

Upgradient & Downgradient Wells

In Barrier (Distribution)

Visual changes

Measurable geochemistry

- *S04, N03, EC, Sodium*

Contaminants

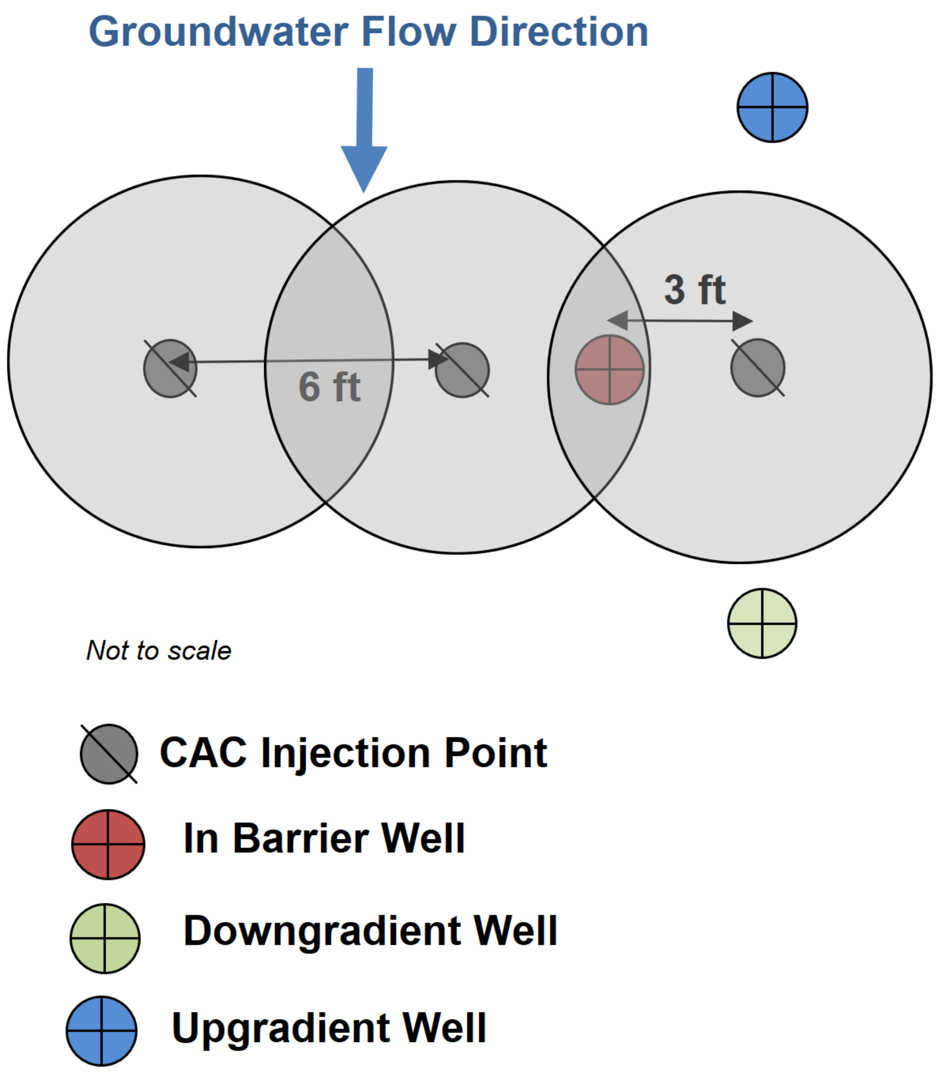
Microbial Indicators

- *QuantArray Petro*

Methane

UIC parameters

Any required



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Post Injection Sampling

- Avoid collecting groundwater samples still black with PetroFix
- PetroFix clarifies in weeks to months to clear or light grey
- If you can see through a VOA and color is light grey, good for sampling
- Post Sampling Technical Bulletins at www.petrofix.com/resources

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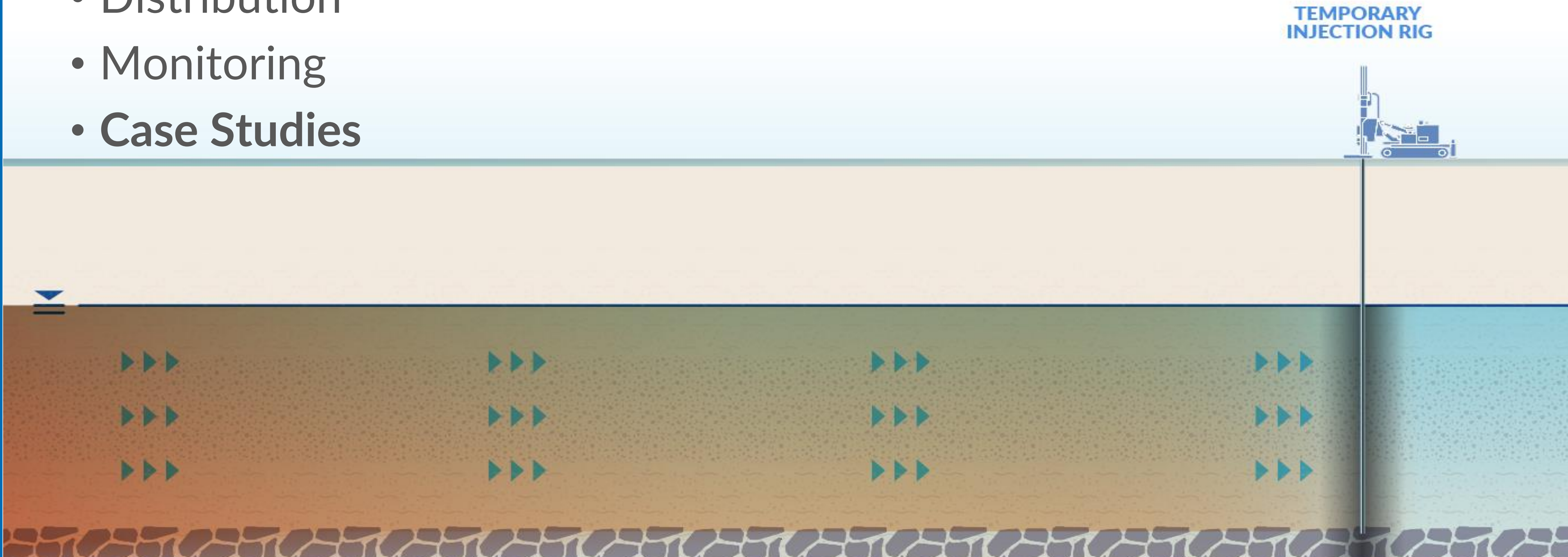

Barrier Protects San Diego Bay

Naval Base Point Loma, San Diego

- Diesel-range plume migrating from fuel storage UST to San Diego Bay
- Install a barrier to intercept TPH-d plume
- January 2021 – 3 injection points to verify distribution in flux zones
- Immediately followed full scale:
  - 46 points
  - Double row, staggered
  - 8 to 18’ bgs
  - 281 gallons per point

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Barrier Protects San Diego Bay

- **Groundwater quality was protected.** TPH-d concentrations decreased to ND in the sentry wells adjacent to San Diego Bay for all 5 post-injection monitoring events (14 months)

- **Nitrate and sulfate concentrations increased** in some wells, stabilized and then decreased to meet water quality parameters for waste discharge compliance within acceptable ranges.

- **Methane concentrations increased** in wells, which provides evidence of the biostimulation of anaerobic hydrocarbon biodegradation.

UST 105 corrective action implementation

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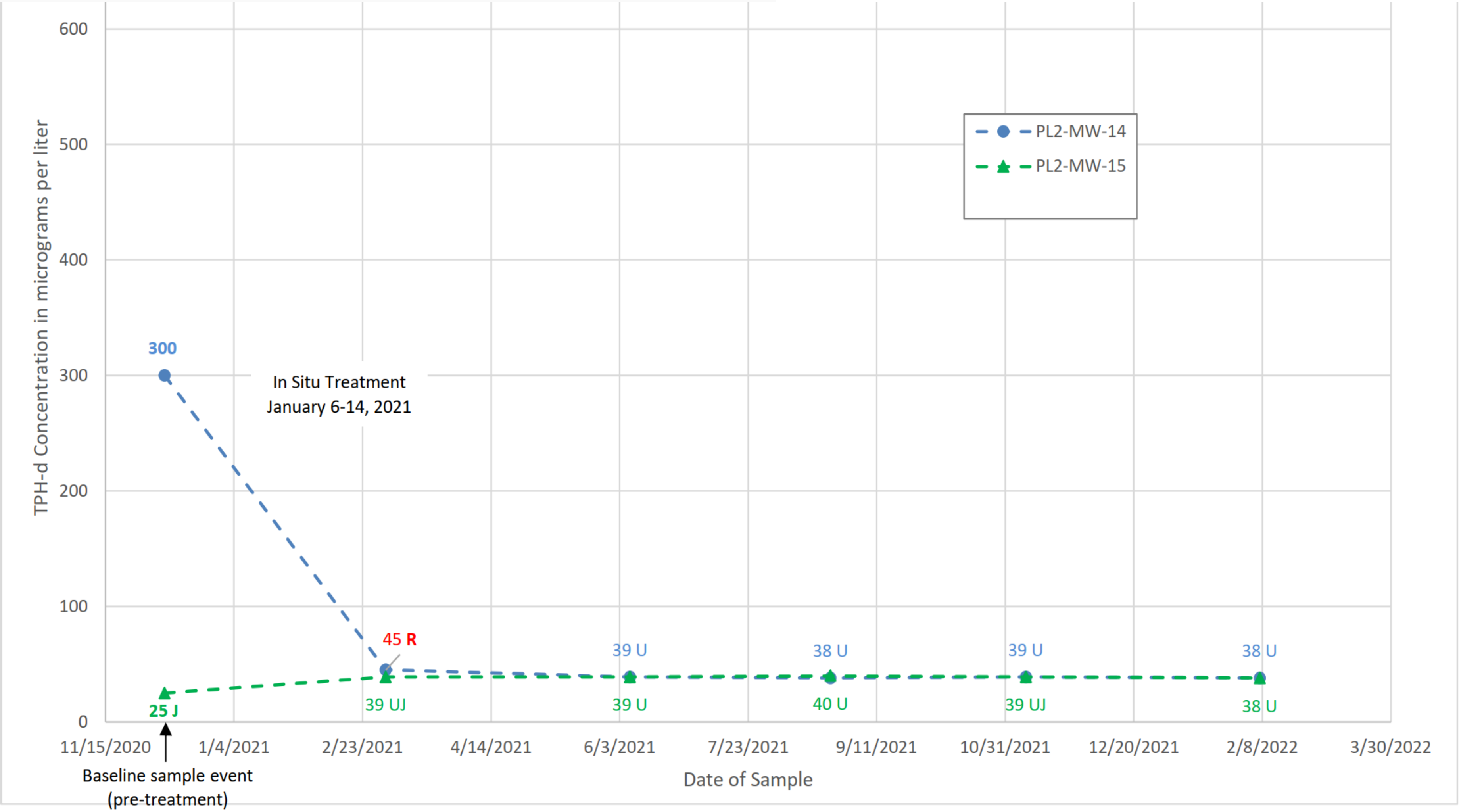
Barrier Protects San Diego Bay



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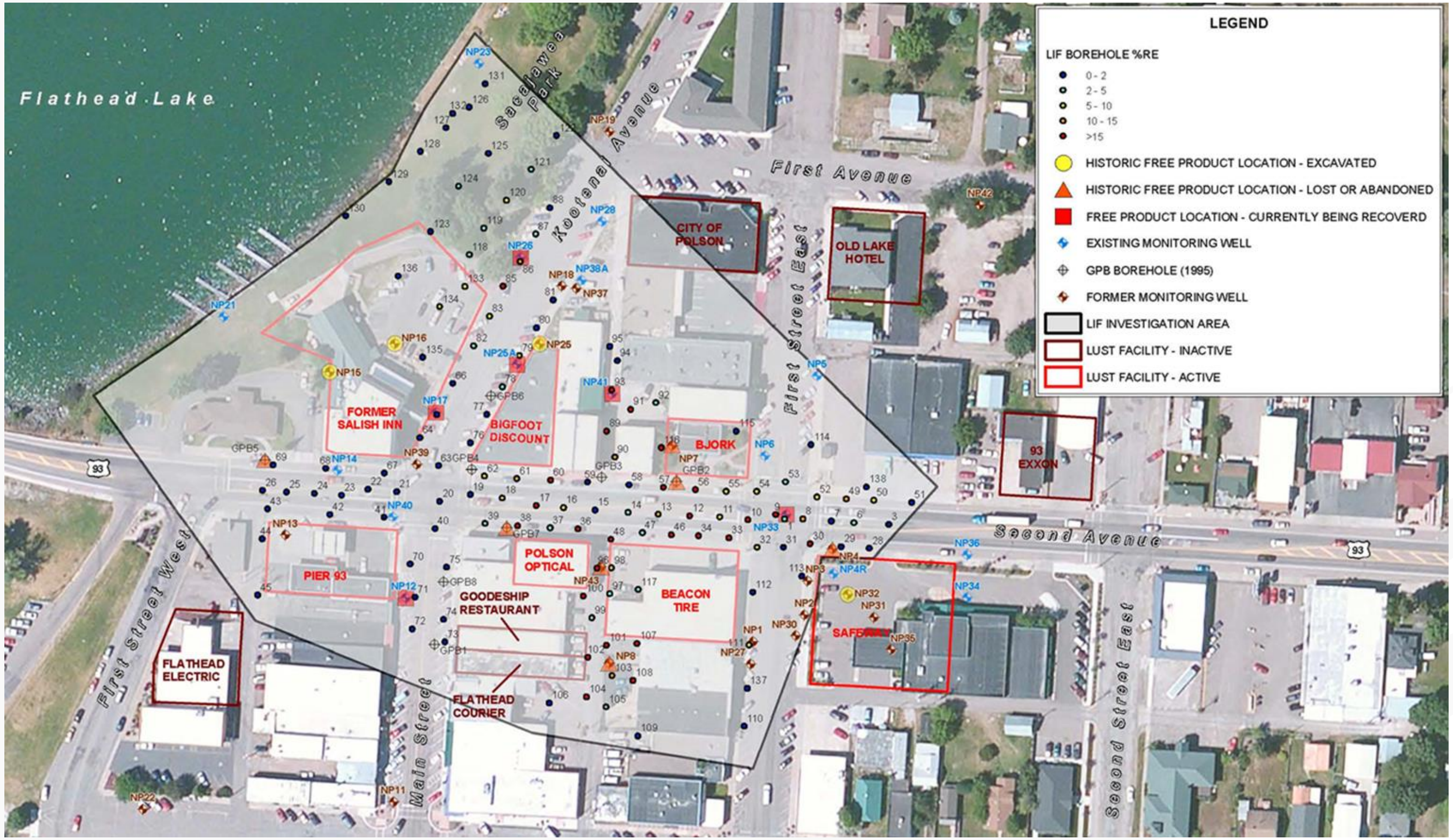
CAC Barrier Protects Flathead Lake, MT

Project Background

- Legacy petroleum release site in downtown Polson, initial investigation in early 1990s
- 13 facilities with releases and individual PRP ownership
- Large undefined LNAPL plume, LNAPL present in various monitoring wells across the site
- Complex lithology consisting of fine-grained, varved lakebed sediments
- Sensitive surface water receptor (Flathead Lake)

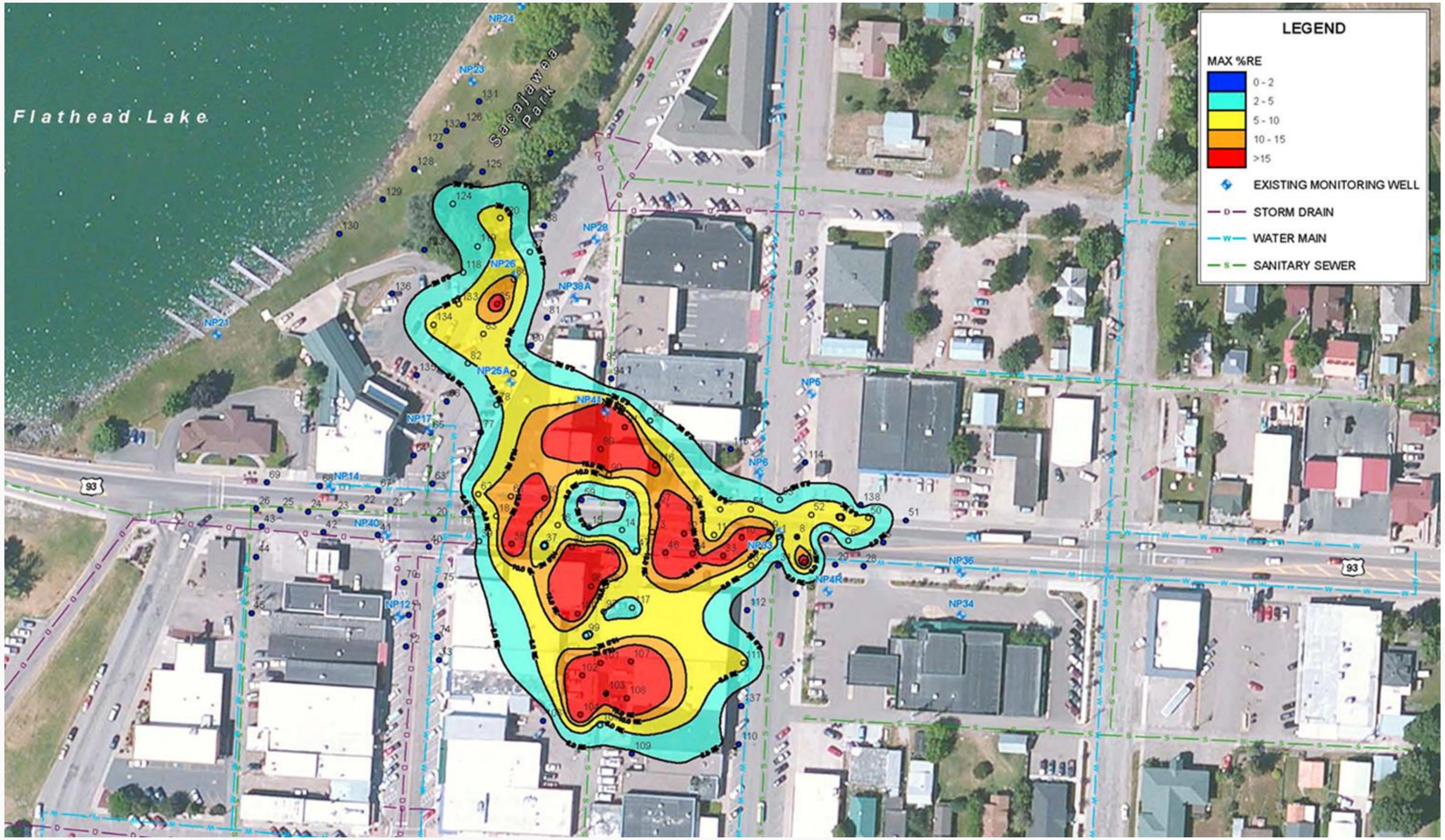
Flathead Lake Reactive CAC Barrier

CSM Development – High Resolution Site Characterization (HRSC)



Flathead Lake Reactive CAC Barrier

CSM Development – HRSC Investigation



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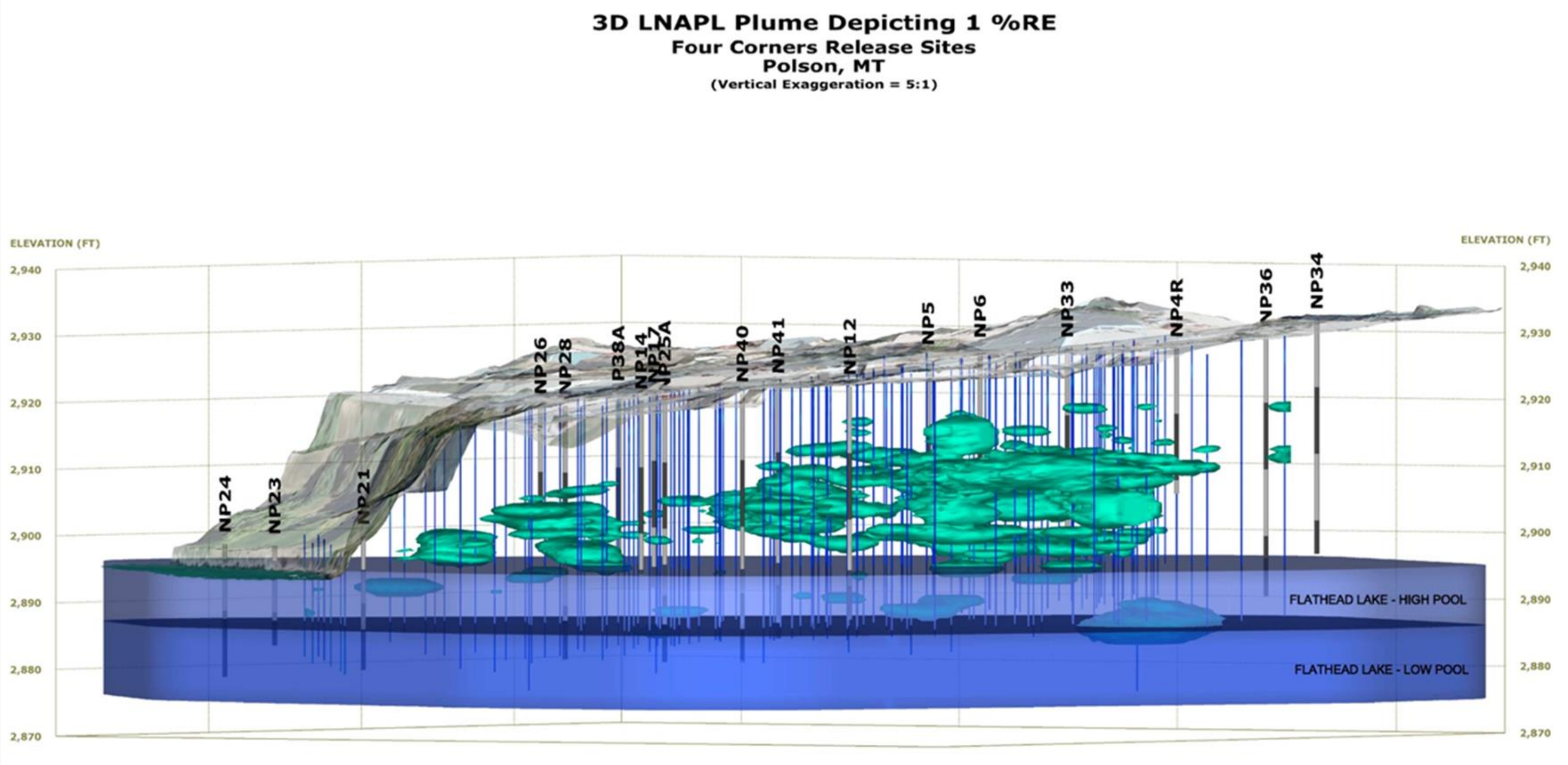
Flathead Lake Reactive CAC Barrier

CSM Development – HRSC Investigation



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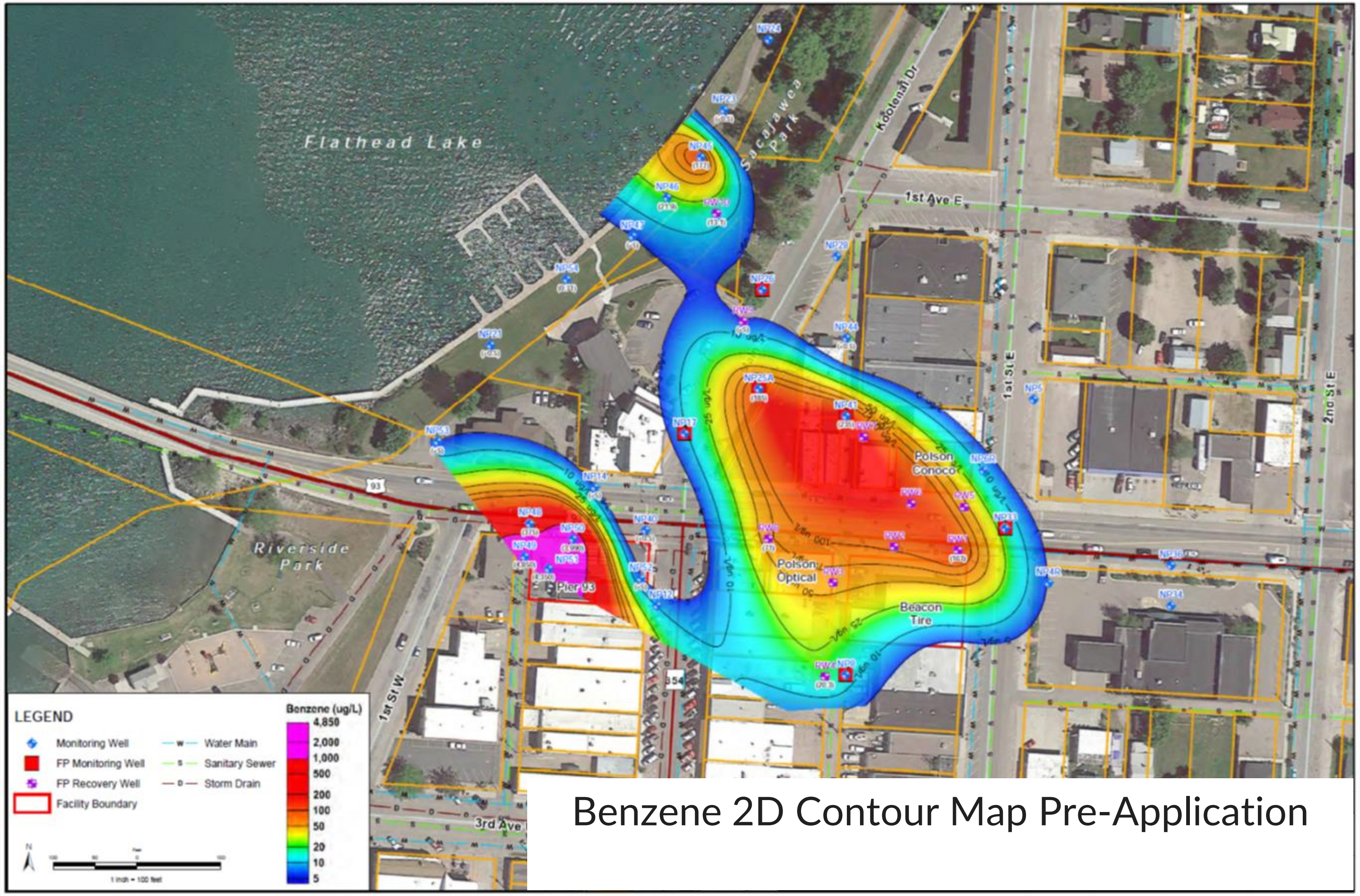
Flathead Lake Reactive CAC Barrier



Benzene 2D Contour Map Pre-Application

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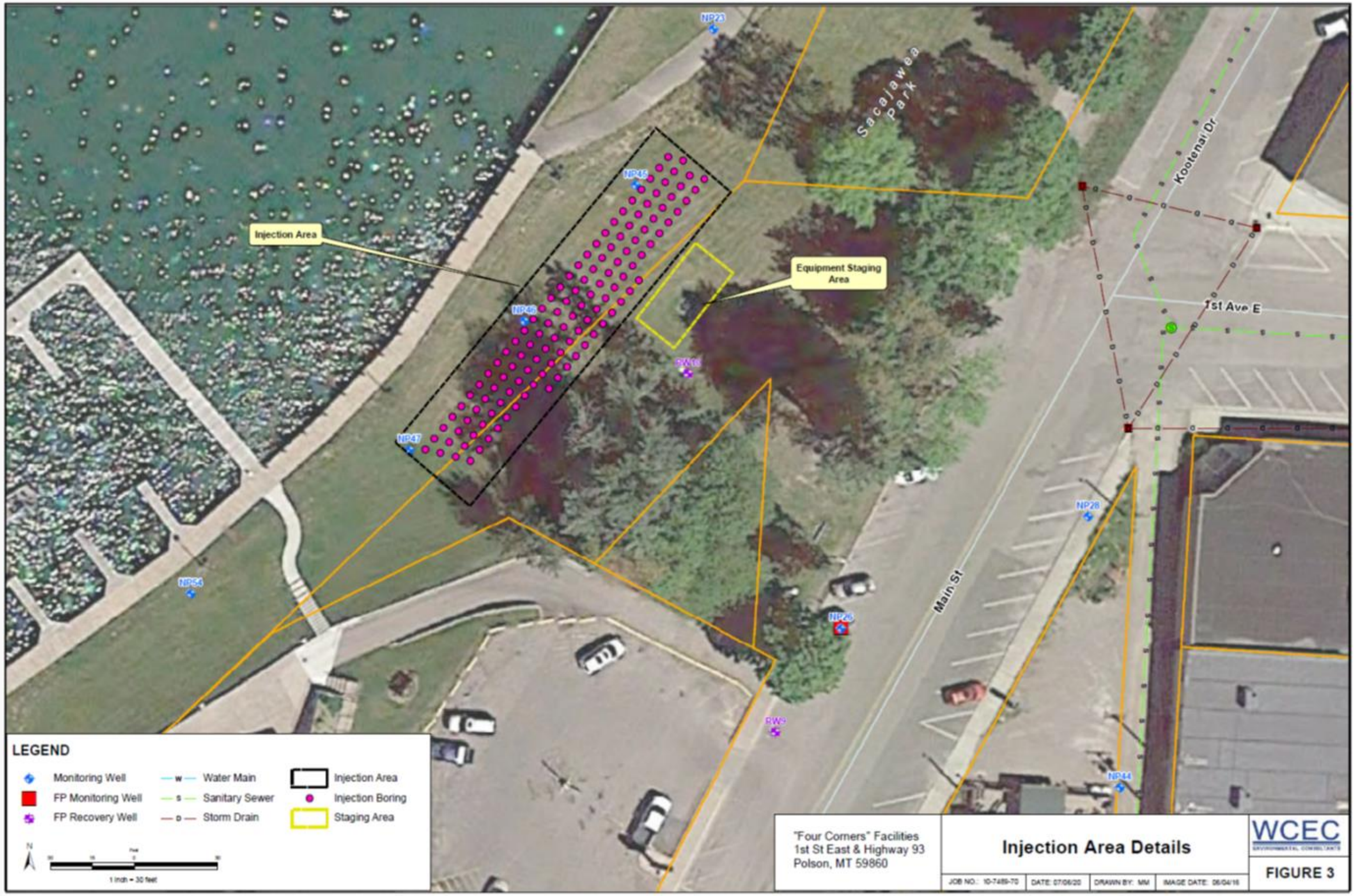
Flathead Lake Reactive CAC Barrier



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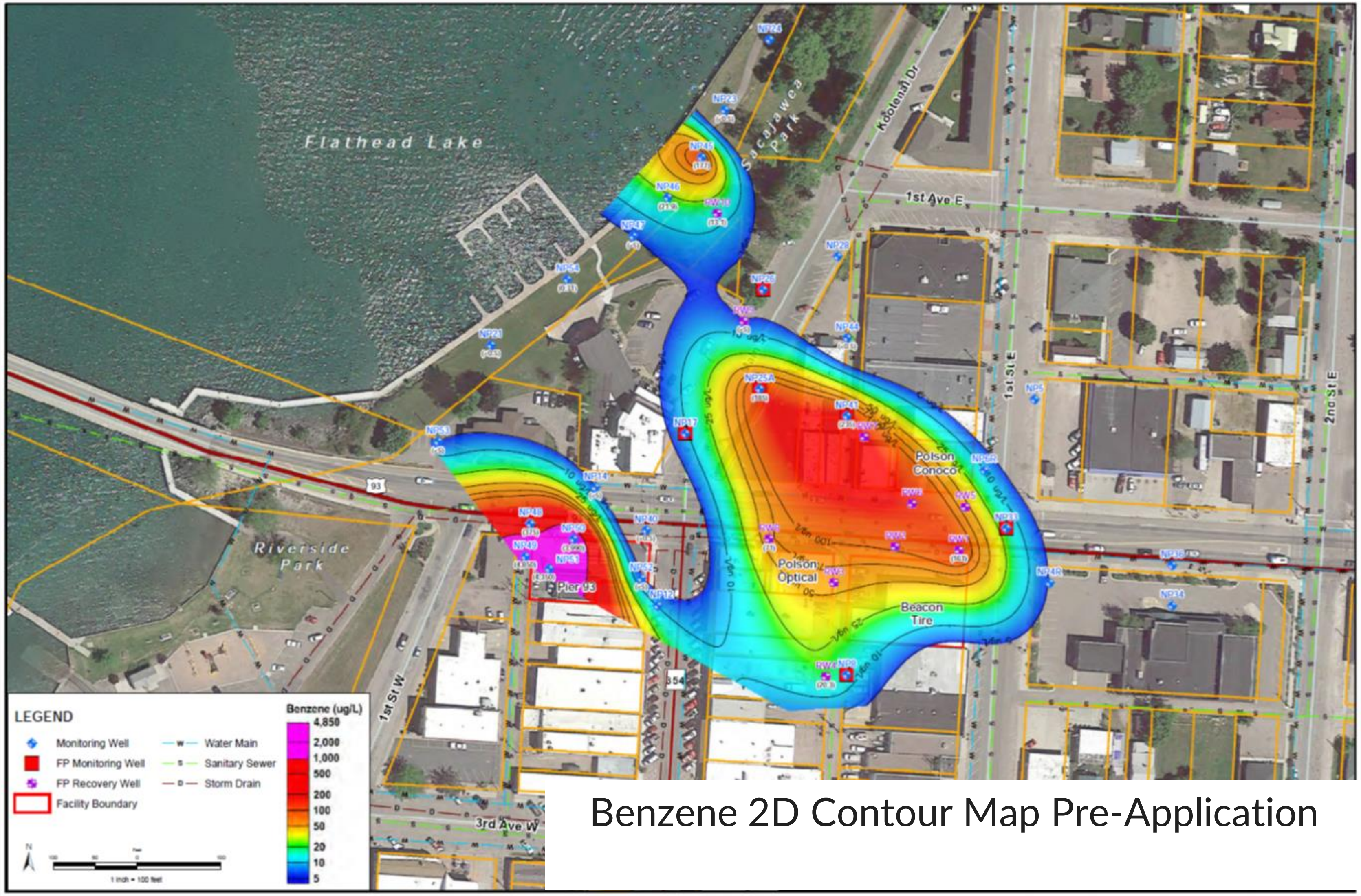
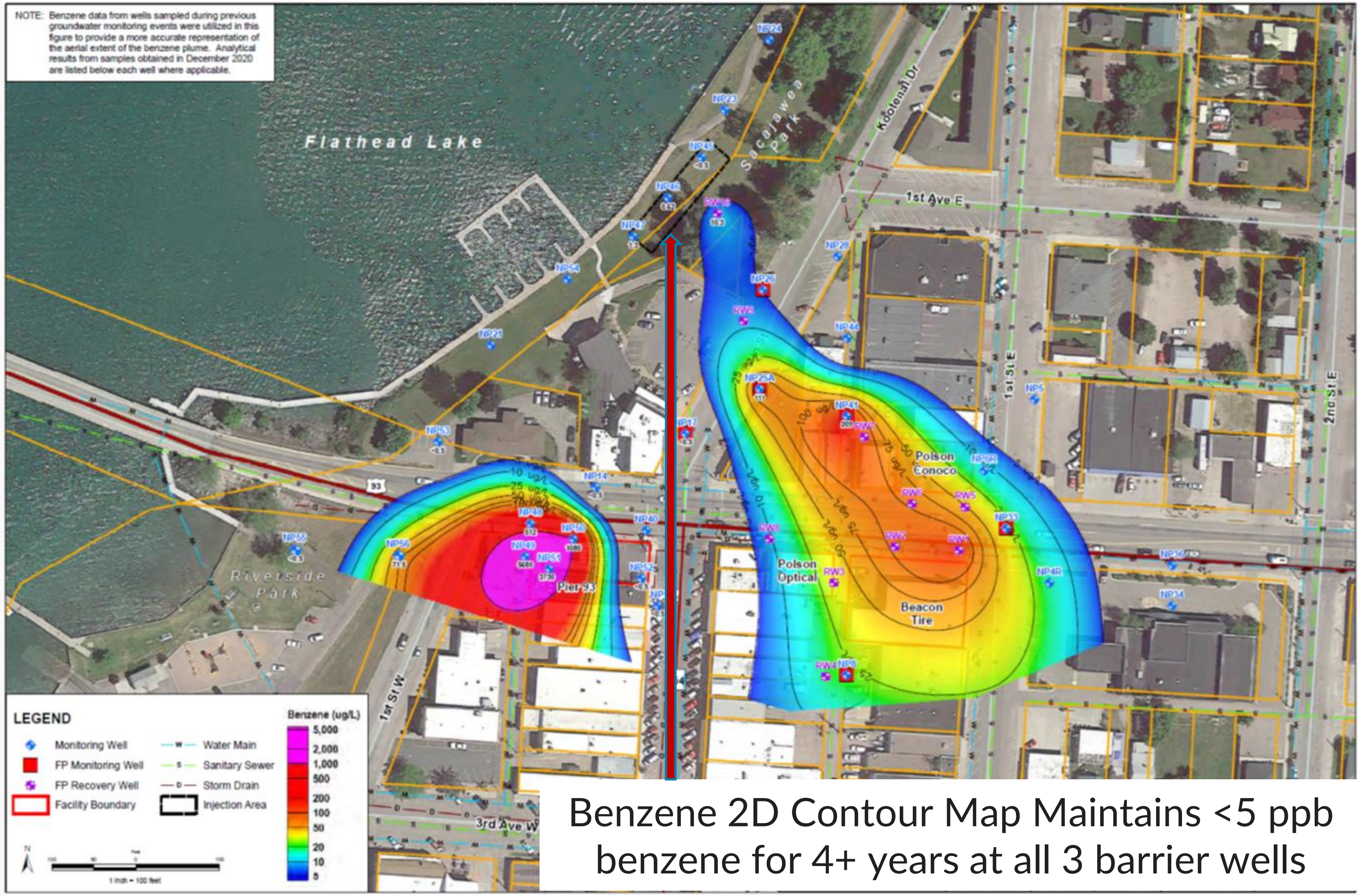
Flathead Lake Reactive CAC Barrier



Benzene 2D Contour Map Pre-Application

Flathead Lake Reactive CAC Barrier



Benzene 2D Contour Map Maintains <5 ppb benzene for 4+ years at all 3 barrier wells

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Colloidal Barrier Conclusions

Results:

- CAC can form long-term bio-regenerative barriers
- Mass flux is important for the Remedial Conceptual Model (RCM)
- Field distribution verification is key
- Rapidly effective
- Low concentrations can be achieved (to ND)
- Safe for wells

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Questions?

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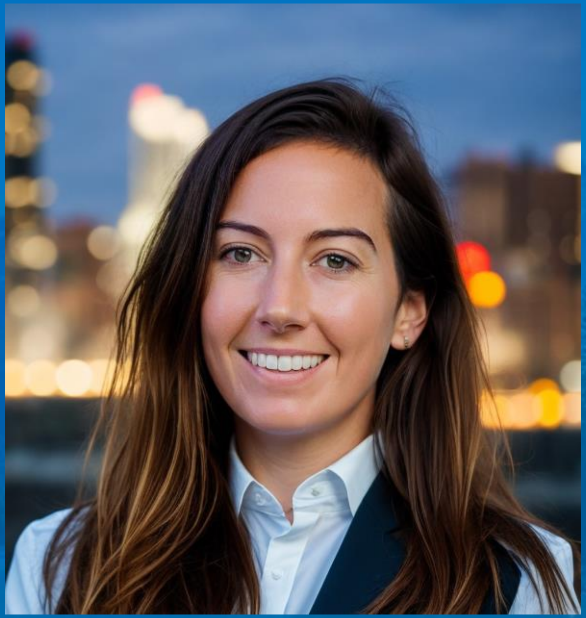

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