# Natural Source Zone Depletion and the Activated Carbon Remedy: Friend or Foe

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# Natural Source Zone Depletion (NSZD)

LNAPL is degraded via naturally occurring processes of biodegradation, volatilization, and dissolution. The predominant process is **biodegradation**, including direct LNAPL-contact biodegradation. LNAPL constituents dissolve, biodegrade, volatilize, solubilize in soil moisture, and also subsequently biodegrade in the vadose zone. Biodegradation produces gaseous products, such as methane and carbon dioxide and ultimately completely mineralize the LNAPL.

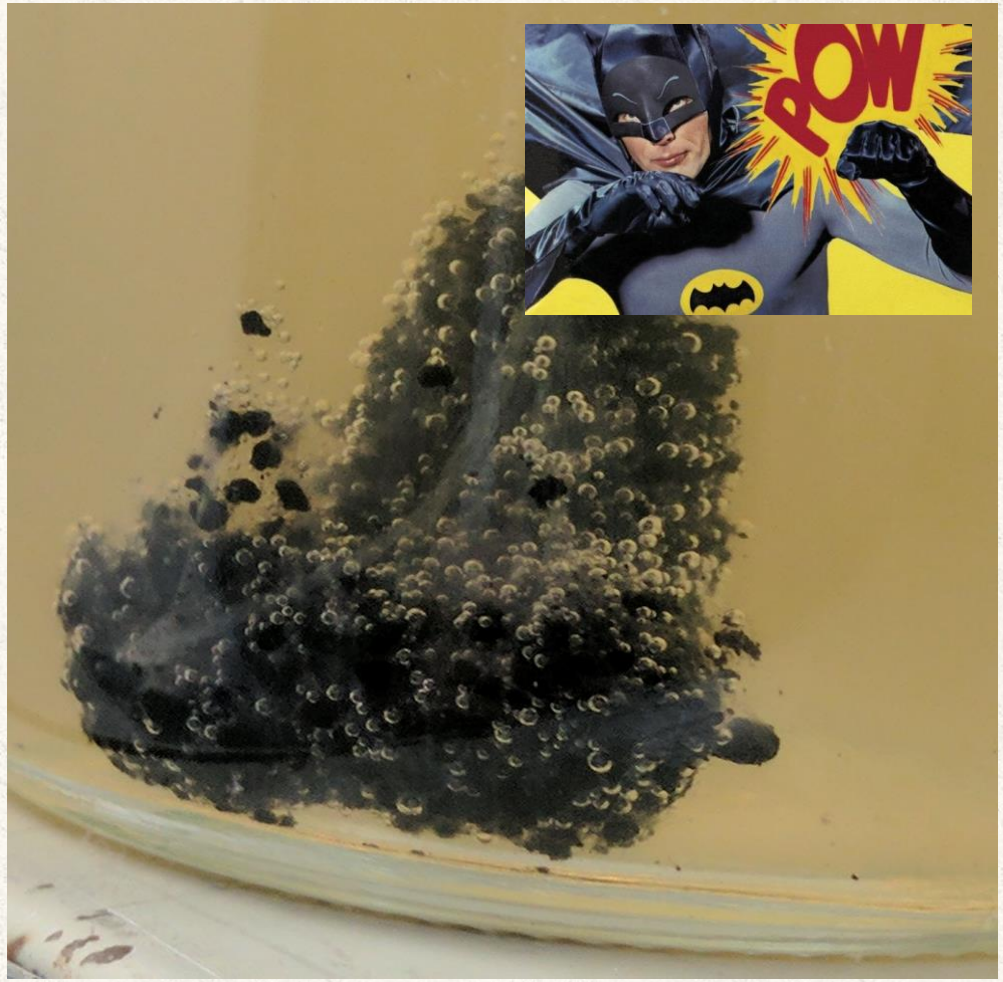
(Source: LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies, ITRC)

# More from ITRC

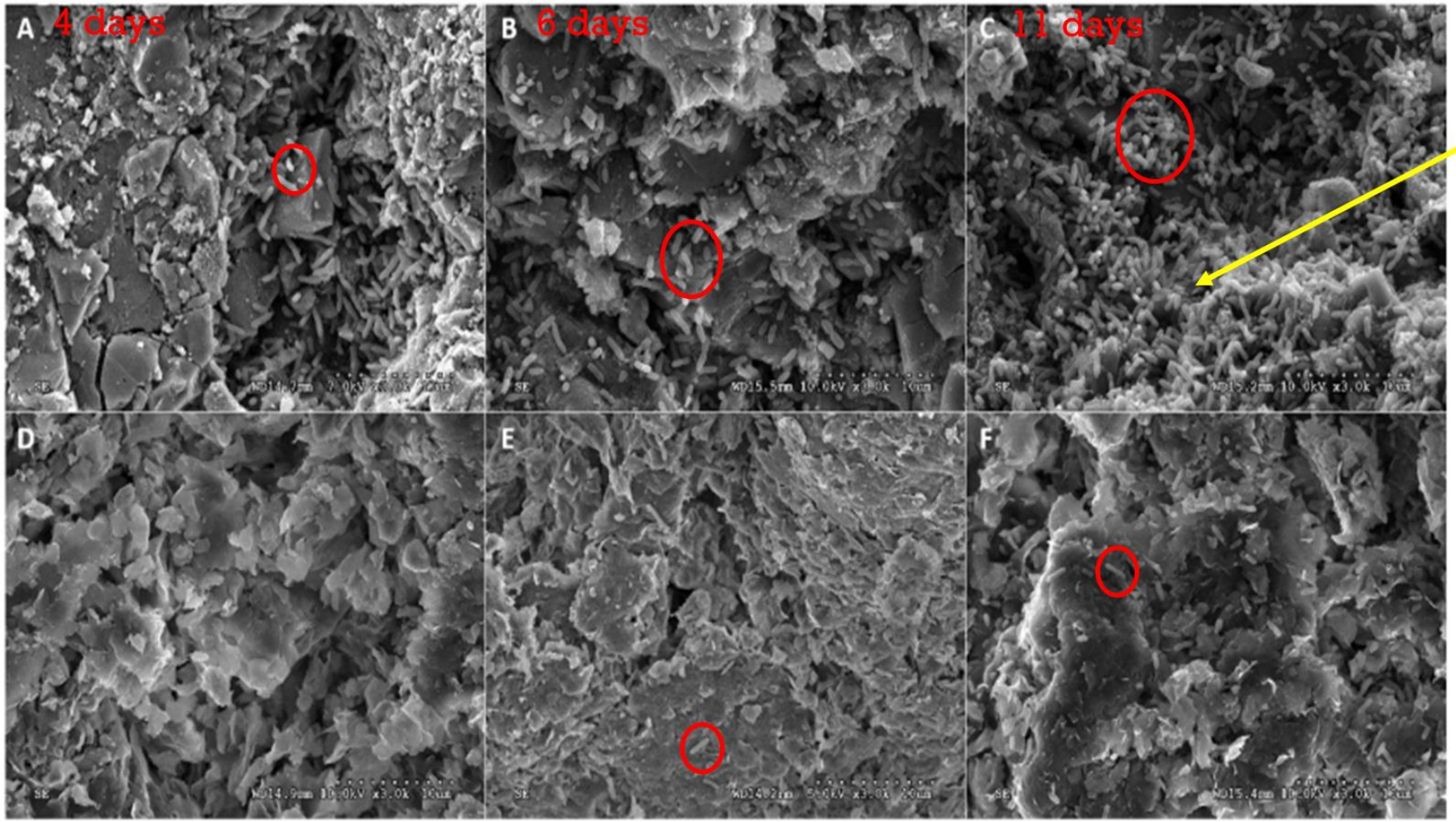
- Once released into the subsurface, hydrocarbon constituents in LNAPL undergo various processes that reduce the total LNAPL mass.
- LNAPL NSZD occurs when certain processes act to (a) **physically redistribute** LNAPL components and (b) **biologically break down** NAPL components.
- Specifically, these processes involve:
  - i) **sorption,** dissolution, volatilization, and biodegradation

# So, what role can Activated Carbon (AC) play in enhancing NSZD?

- Physically redistribute
  - Possible through high-energy injection techniques
  - Addition of surfactants may play a role
- Sorption
  - LNAPL and dissolved PHC mass sorb to the AC pore structure
  - Wait, won't the LNAPL kill off the bacteria?
- Biologically break down (e.g. biodegradation)
  - Bacteria adhere to AC and reside with the macropore and micropore "niches" in the carbon matrix
  - Dissolved gases such as $CO_2$ and $CH_4$ can be used to monitor the degradation progress/rates

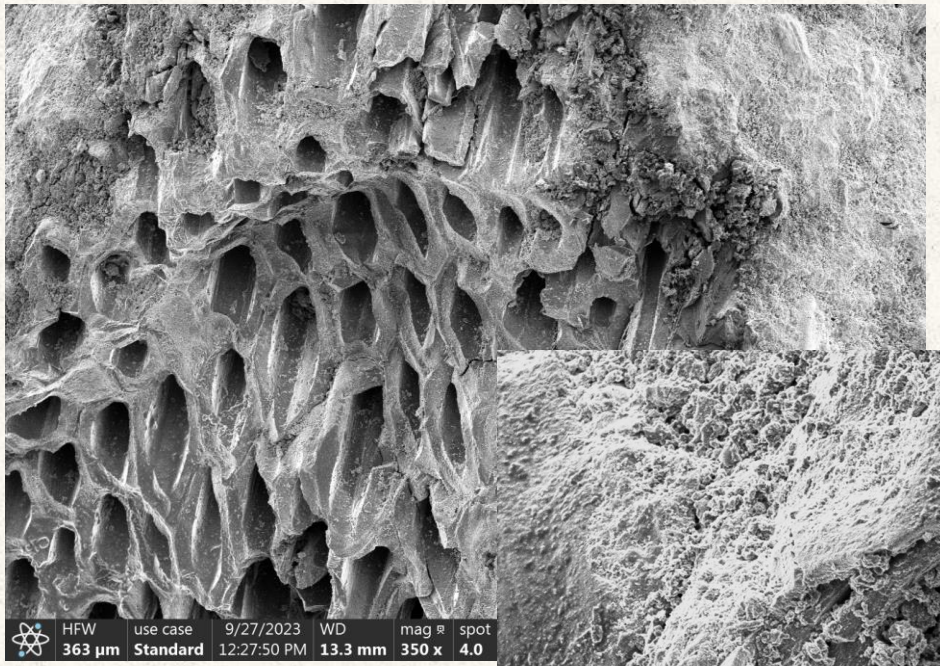


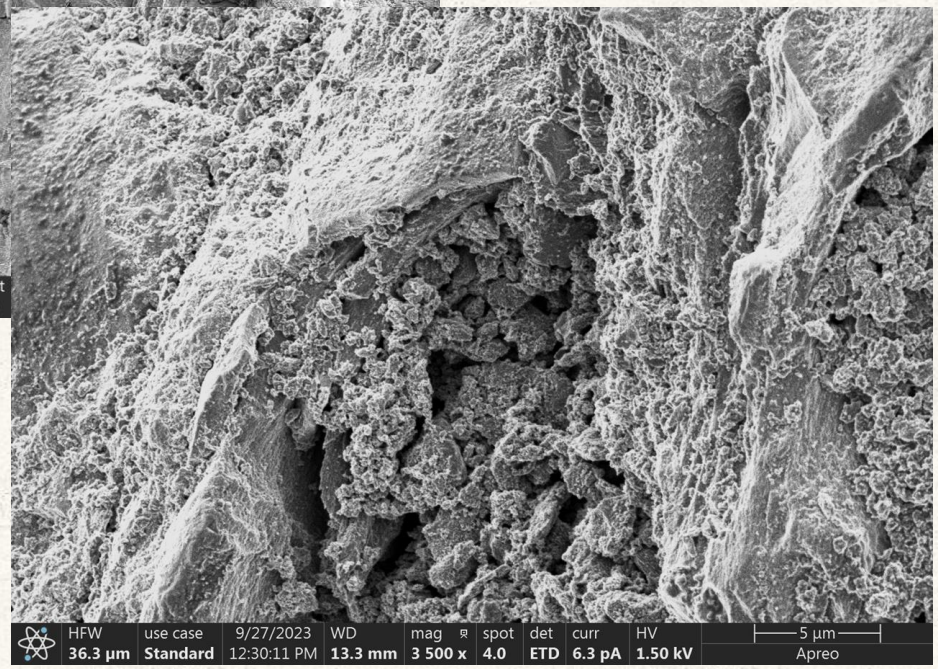
# Microbial growth on AC is more abundant than on clays, silts, and other geomaterials.



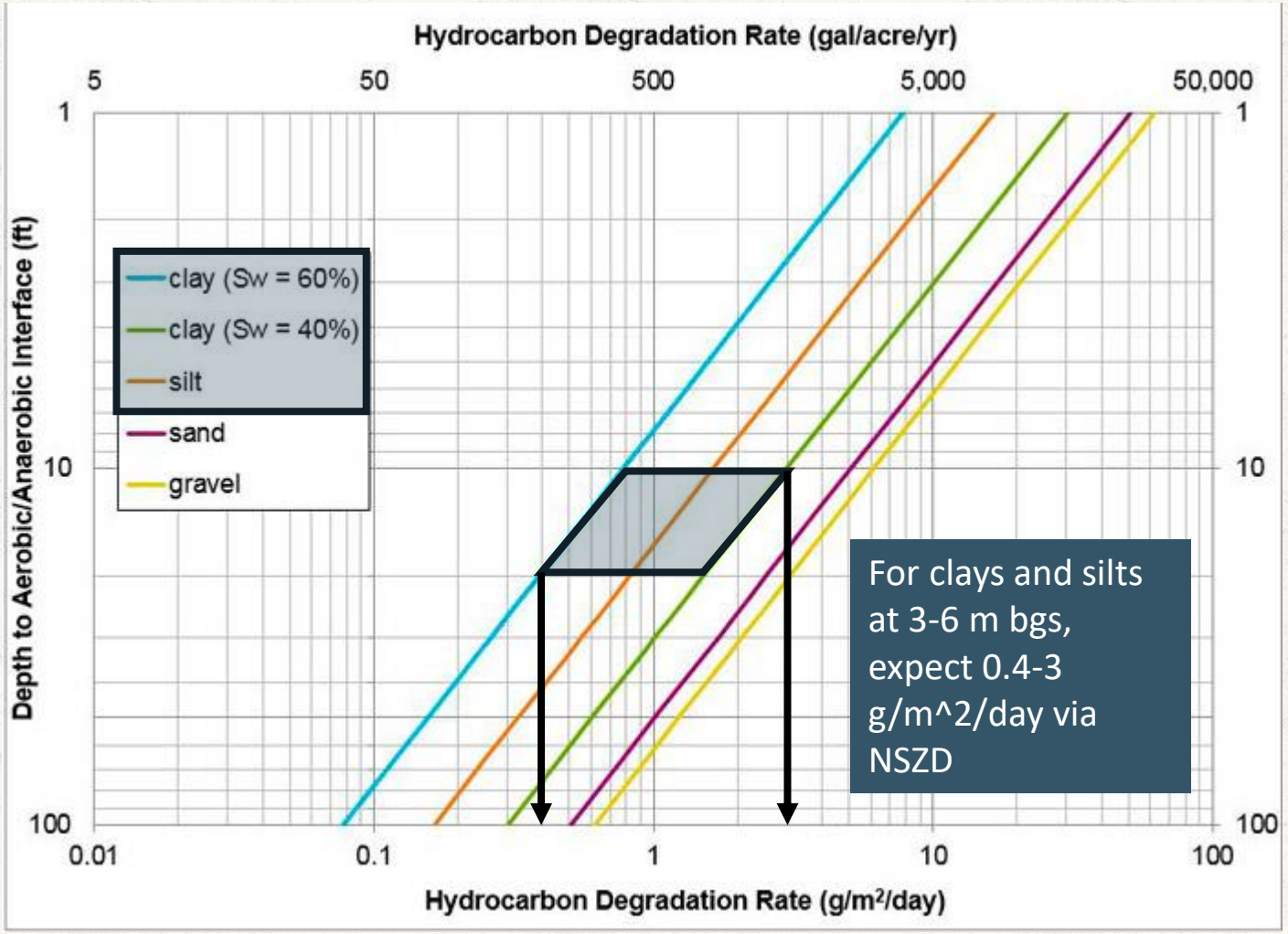

Pagnozzi, 2020

# Coal v. Wood Based Carbon Comparison

# NSZD Degradation Rates



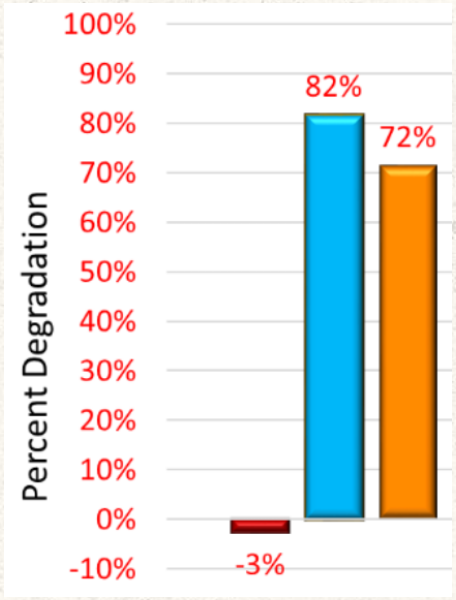

ITRC, 2018

# Step One – Bench Testing

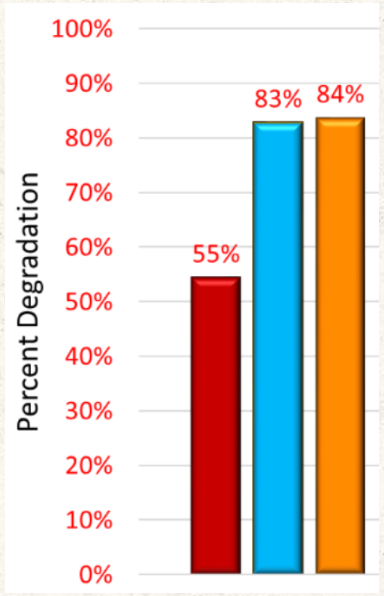
- Bench testing involving both GRO and DRO
  - Varying terminal electron acceptors (e.g. NO3, SO4)
  - Addition of complex carbohydrates
  - Varying types of AC (e.g. coal vs. wood)
  - Varying bacterial blends


# Bench Test Findings

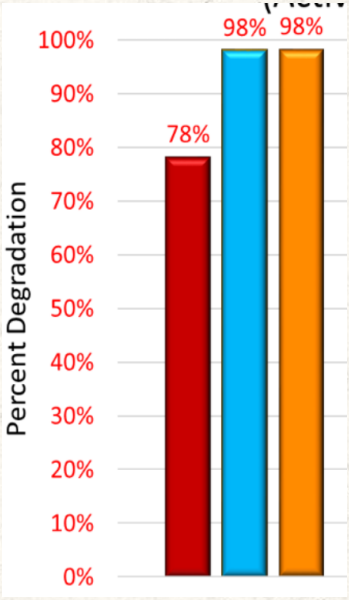
- AC source matters
  - Coal-based carbon was able to adsorb 58% of it's weight as DRO
  - Wood-based 29%
- Electron Acceptor choice matters
  - Tests run for 4 months
- Addition of complex carbohydrate (e.g. starch) increased degradation %




Nitrate only



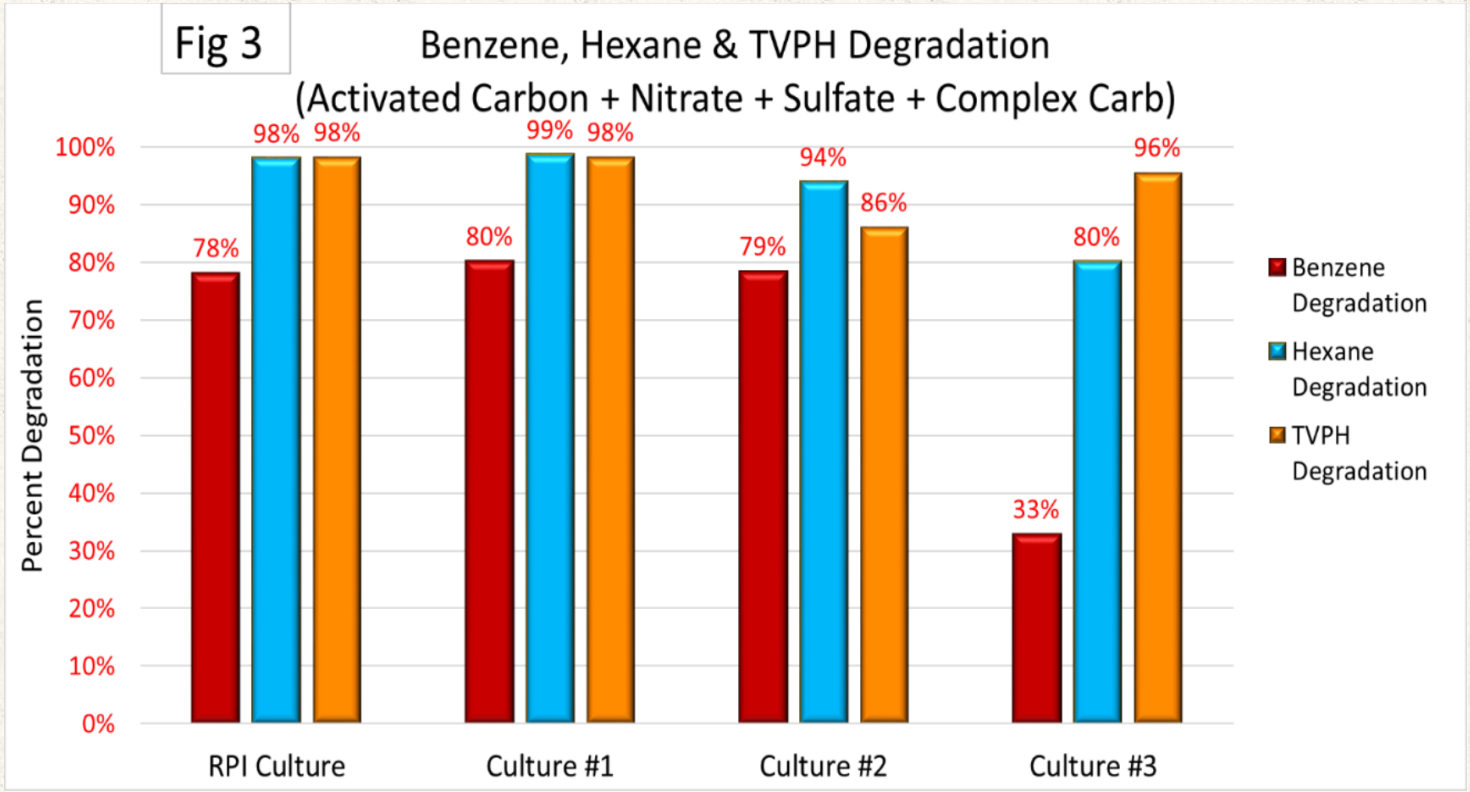

Nitrate + Sulfate



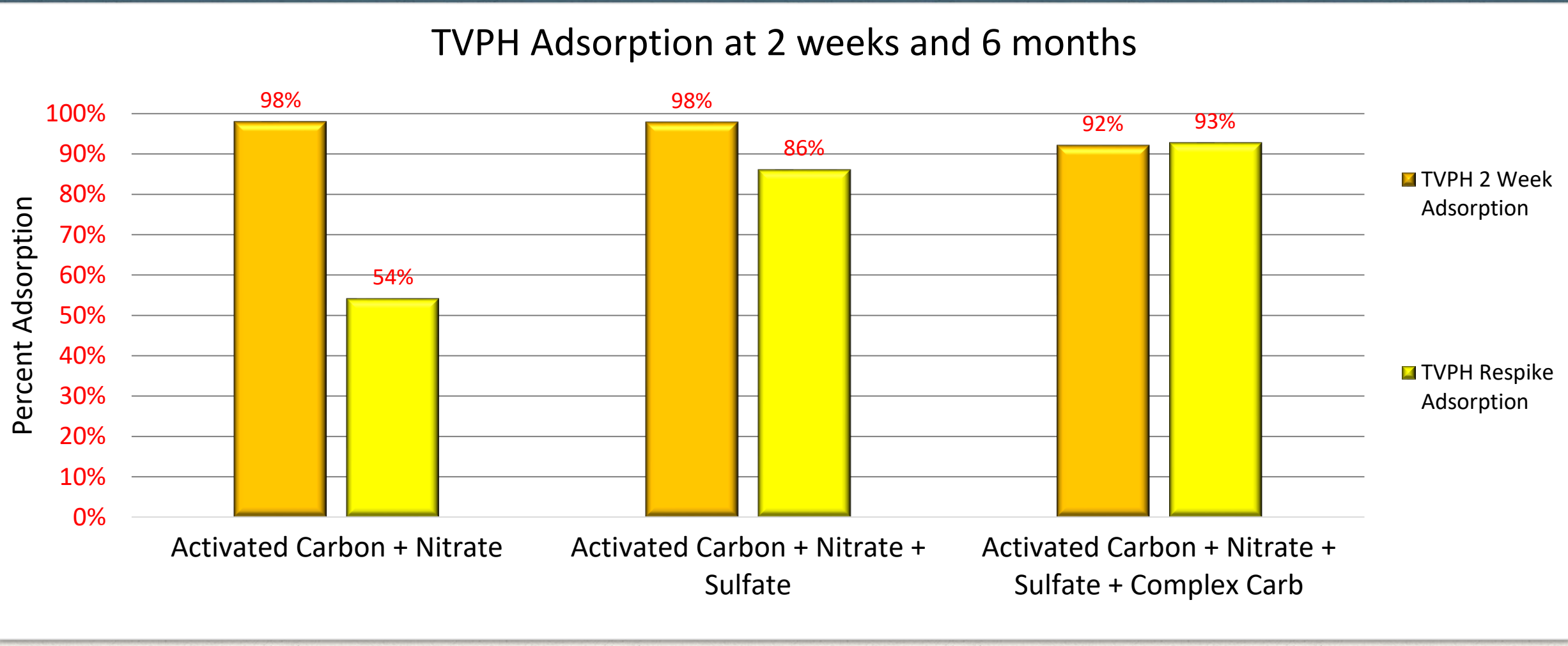

Nitrate + Sulfate + Complex Carb

# Bench Test Findings

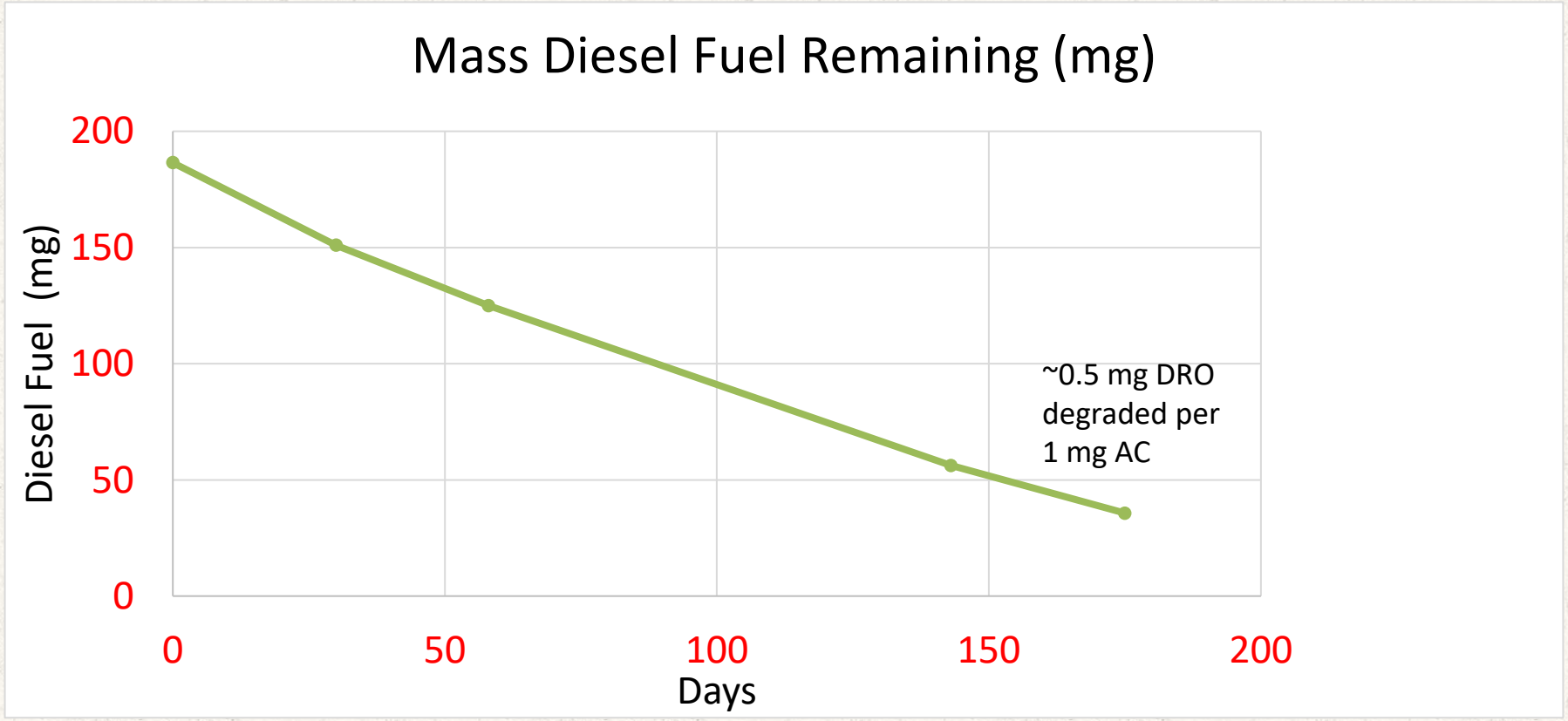
- Bacterial seeding of the carbon is critical to degradation
- Need to have a broad range of PHC degraders
- 3 of the 4 blends tested performed well



# Re-adsorption Experiments

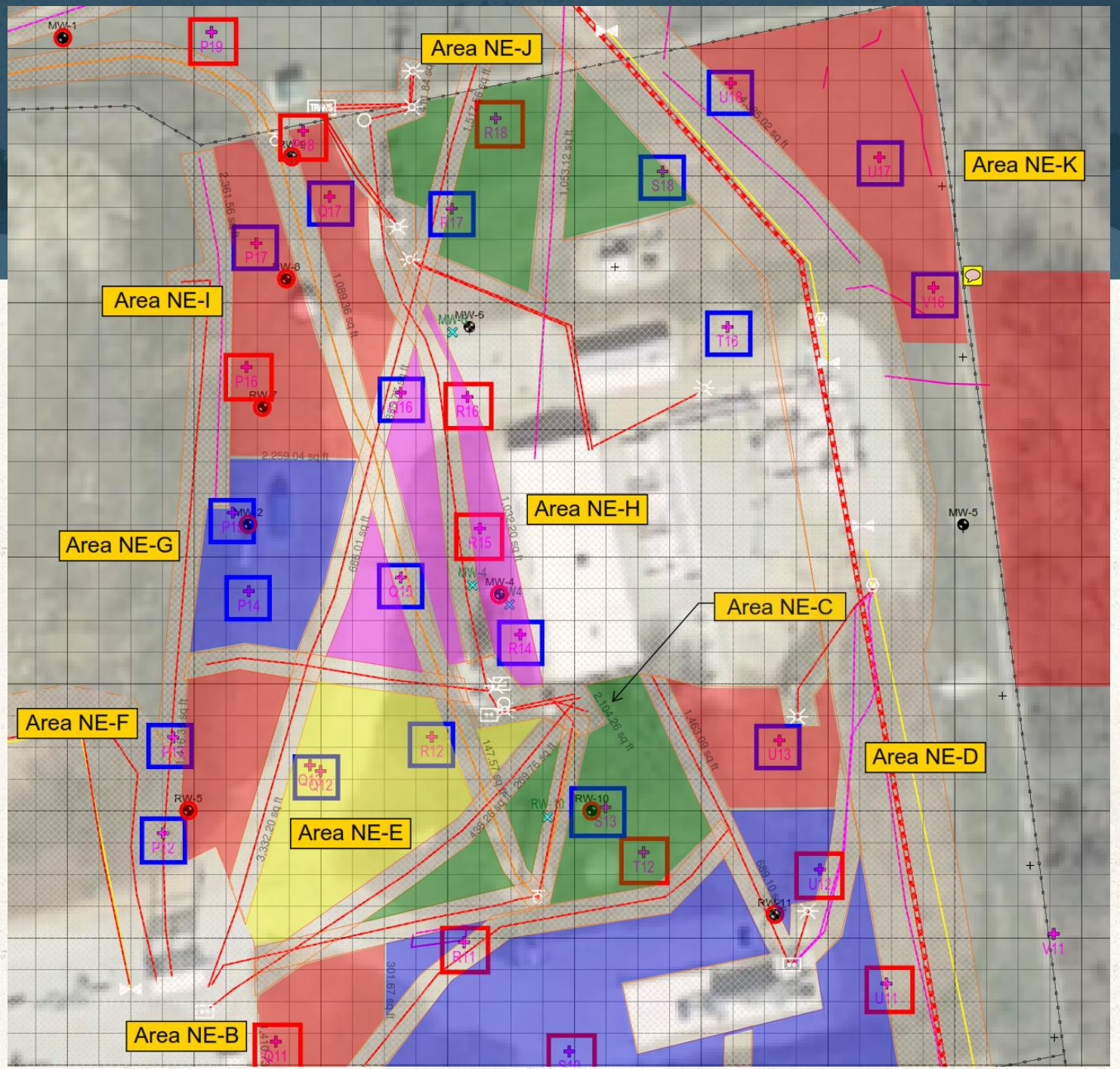


# DRO Degradation Over Time (6 mo)



# Step Two: RDC

- 1,110 soil samples were collected as part of a large RDC
- The sample results were used to create an optimized and surgical AC-based design
- All samples were analyzed at our lab at no cost

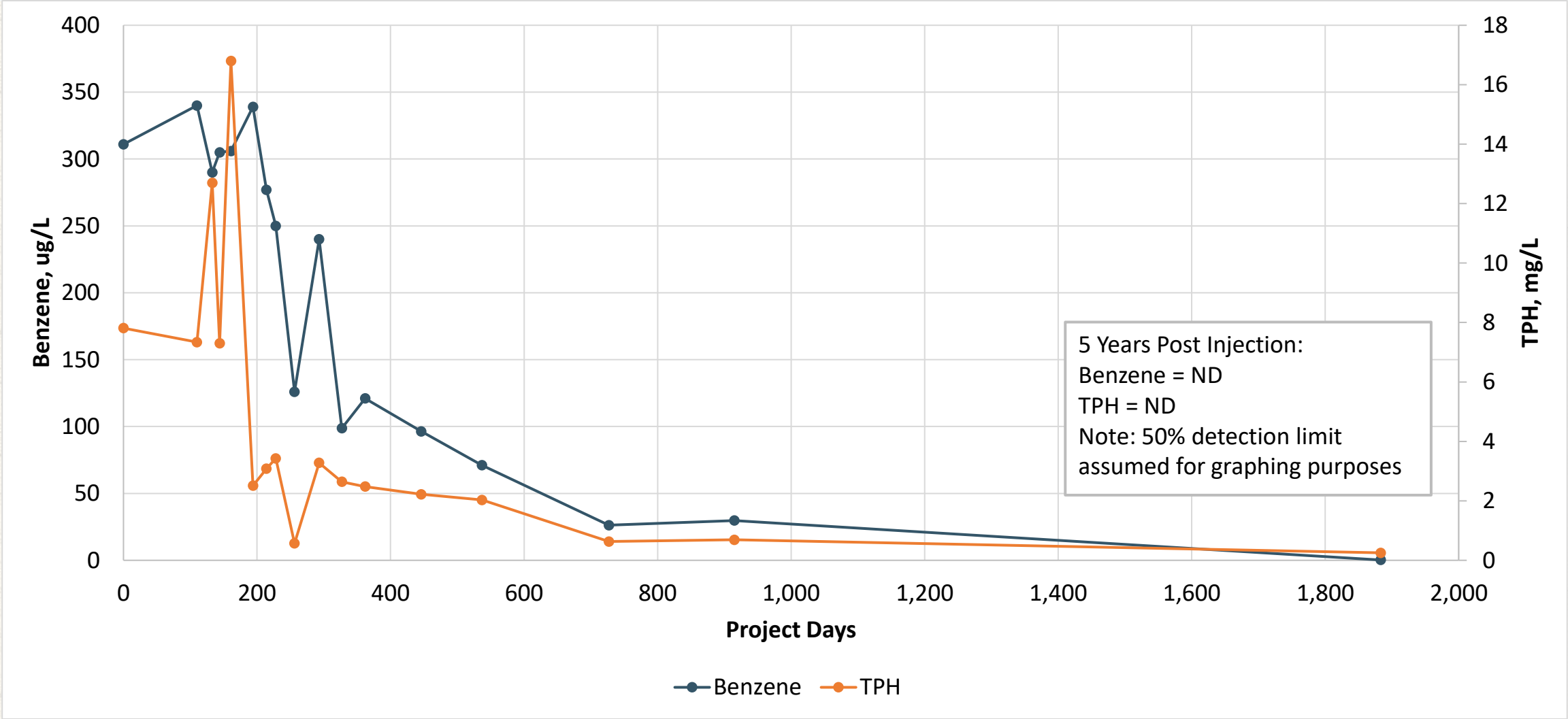


# Step Three – Field Testing

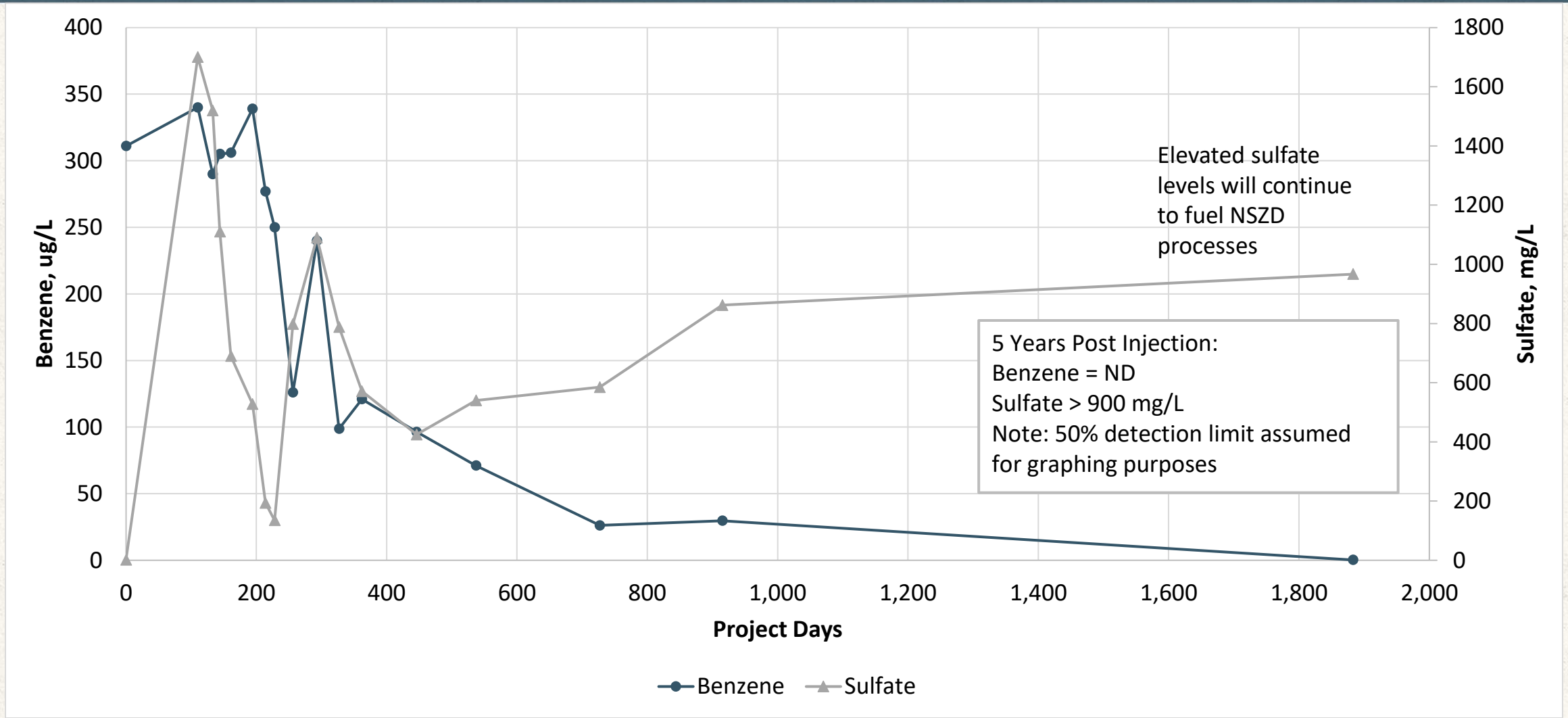
- Treatment Area: 8,650 m2
- Lithology: Varied across the large area but consisted mainly of silty clay to clay over weathered shale with some sand and gravel
- Depth to Water: 1.5 to 6.5 m bgs (variable)
- Contaminants:  LNAPL, TPH, and Benzene
- Technology: AC + TEAs (NO3/SO4) + Complex Carbs + Nutrients + Bacteria
- Implementation Method: Direct push and Pre-Drill injection*

*HSA through weathered shale, backfilled with bentonite, injected like DPT application

# Results: Benzene and TPH

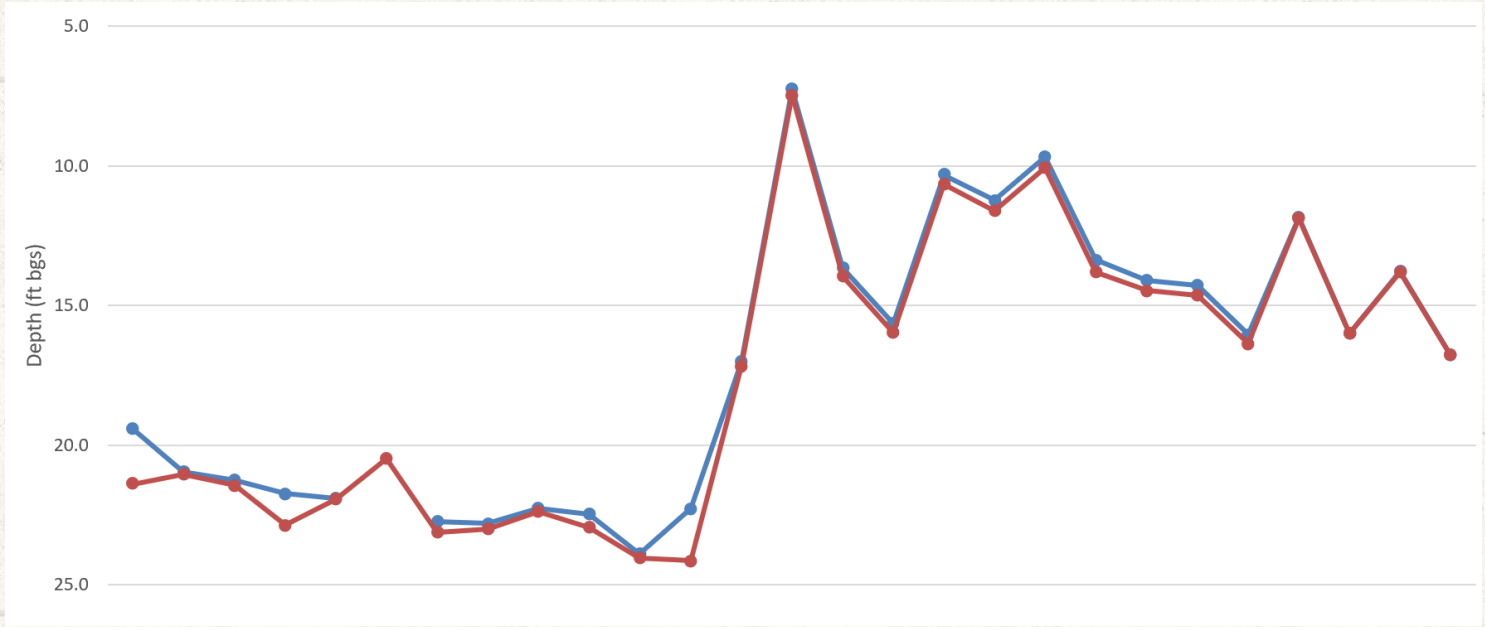


# Results: Benzene and Sulfate

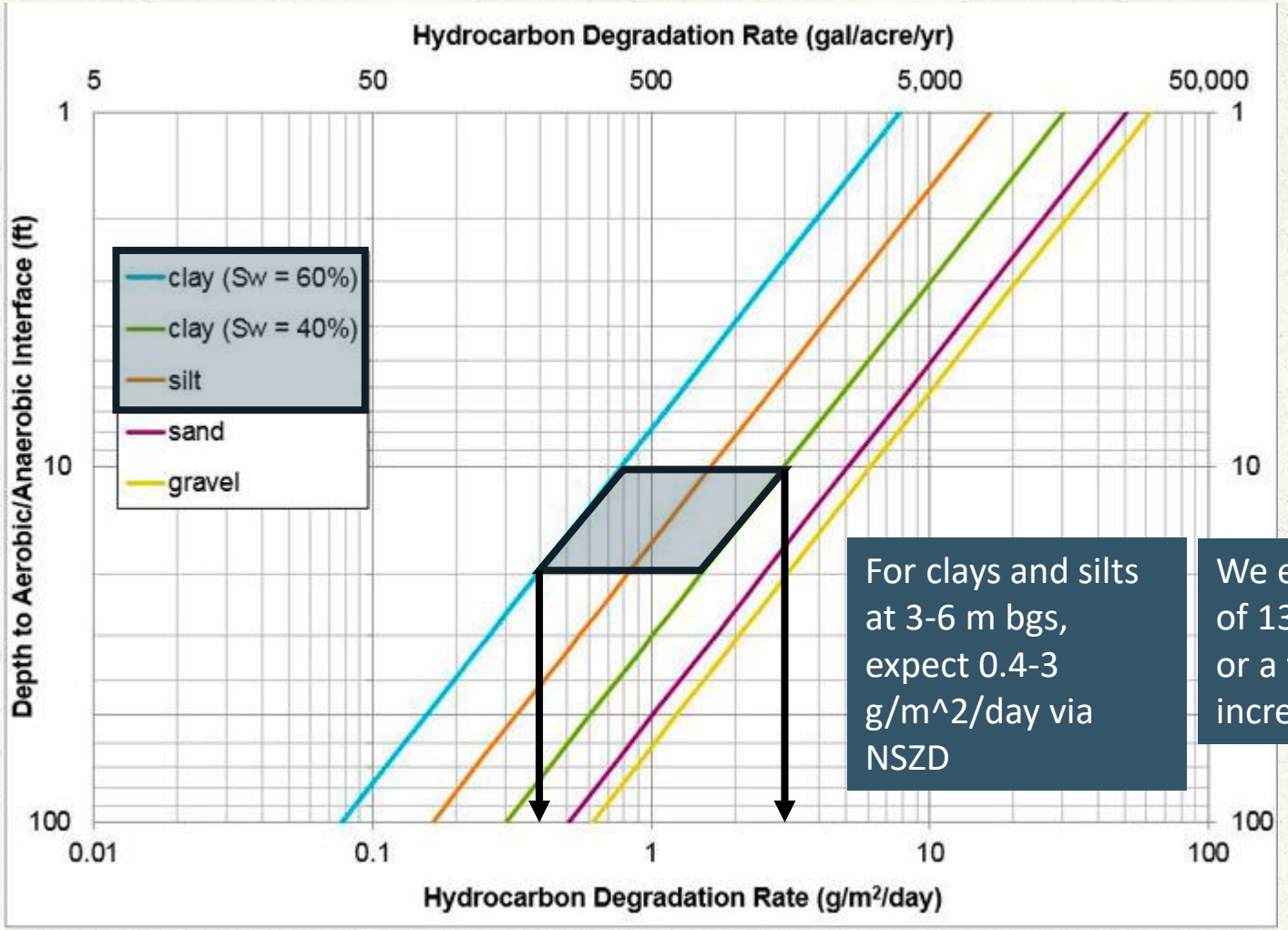


# Results: LNAPL

- LNAPL - The total number of wells with measurable LNAPL prior to remediation: 15
- Post-remediation LNAPL statistics
  - No measurable LNAPL: 12
  - Sheen: 2
  - Measurable LNAPL: 1 (current max LNAPL thickness = 6 mm)



# Results: NSZD Degradation Rates




For clays and silts at 3-6 m bgs, expect 0.4-3 g/m^2/day via NSZD

We estimate a rate of 13.8 g/m^2/day, or a ~5-30x increase

ITRC, 2018

# Summary

- AC can be used to enhance biological degradation of petroleum hydrocarbons and increase NSZD rates
- AC types have different sorption capacities
- The bacteria “regenerate” the carbon in-situ to provide a long-term remediation strategy
- Limiting factor will be long-term terminal electron acceptor (TEA) availability
- Proper CSM development and understanding of total contaminant mass will assist in AC and TEA application rates

# Thank you! Questions?

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