The Rise of New Insitu Soil Blending and Vadose Zone Amendment Strategies to Accelerate Source and Plume Remediation

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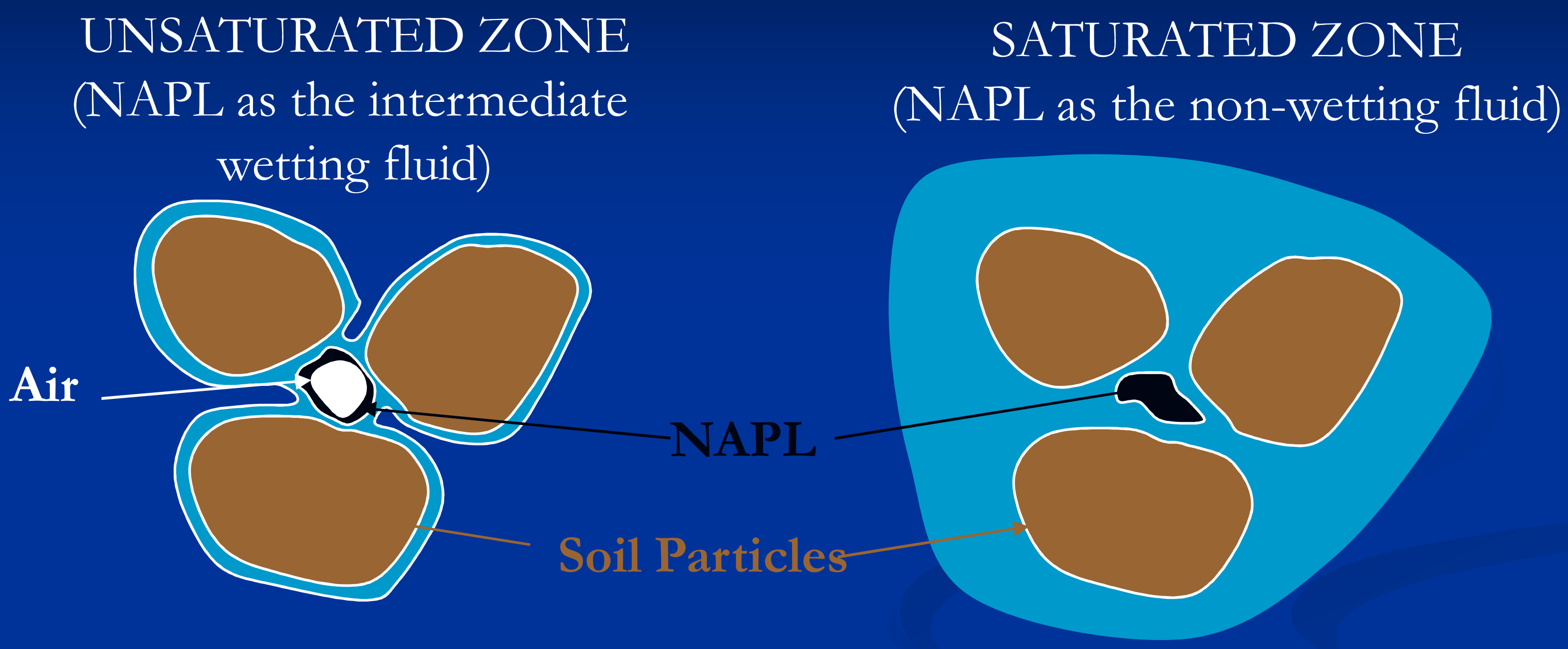
Overview

- Residual contamination and geometric scope
- Remediation Techniques
- Access (injection and blending)
- Case Studies
- Cost

Contaminant Distribution in Subsurface

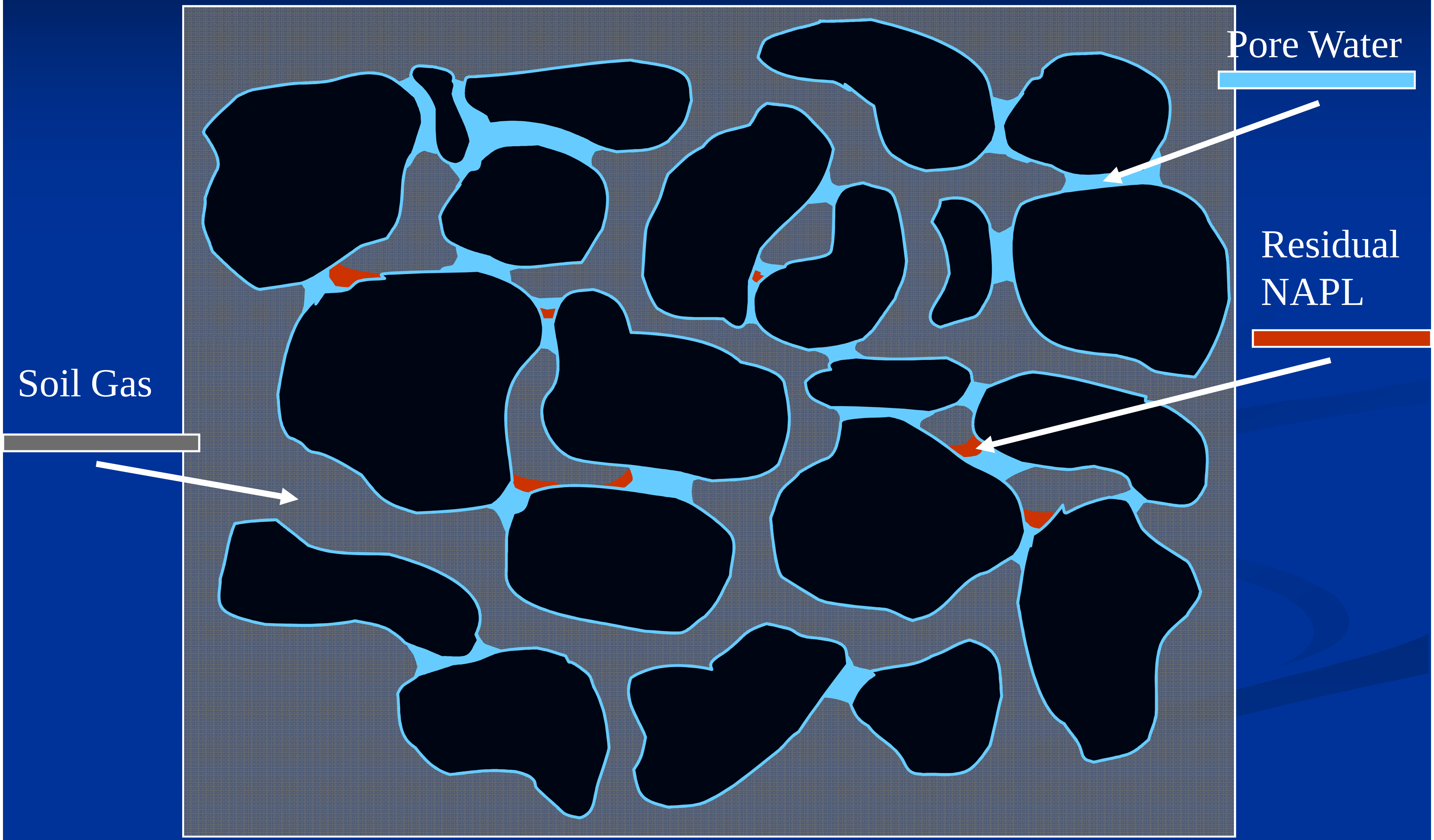
- Contaminants are heterogeneously distributed in a physically (geologic), chemically, and biologically heterogeneous volume which is also dynamic – makes things easy.
  - Tortuous, preferential pathways control with diffusion playing small role
  - matrix diffusion usually much less of an issue than occlusion or inaccessible pores
  - Usually worse in vadose zone because of gas phase

Residual NAPL



Residual NAPL often occurs as disconnected blobs within the pore spaces.

Conceptual Model of Residual NAPL in Vadose Zone



Scale Reality

- Very small signal in large noisy system

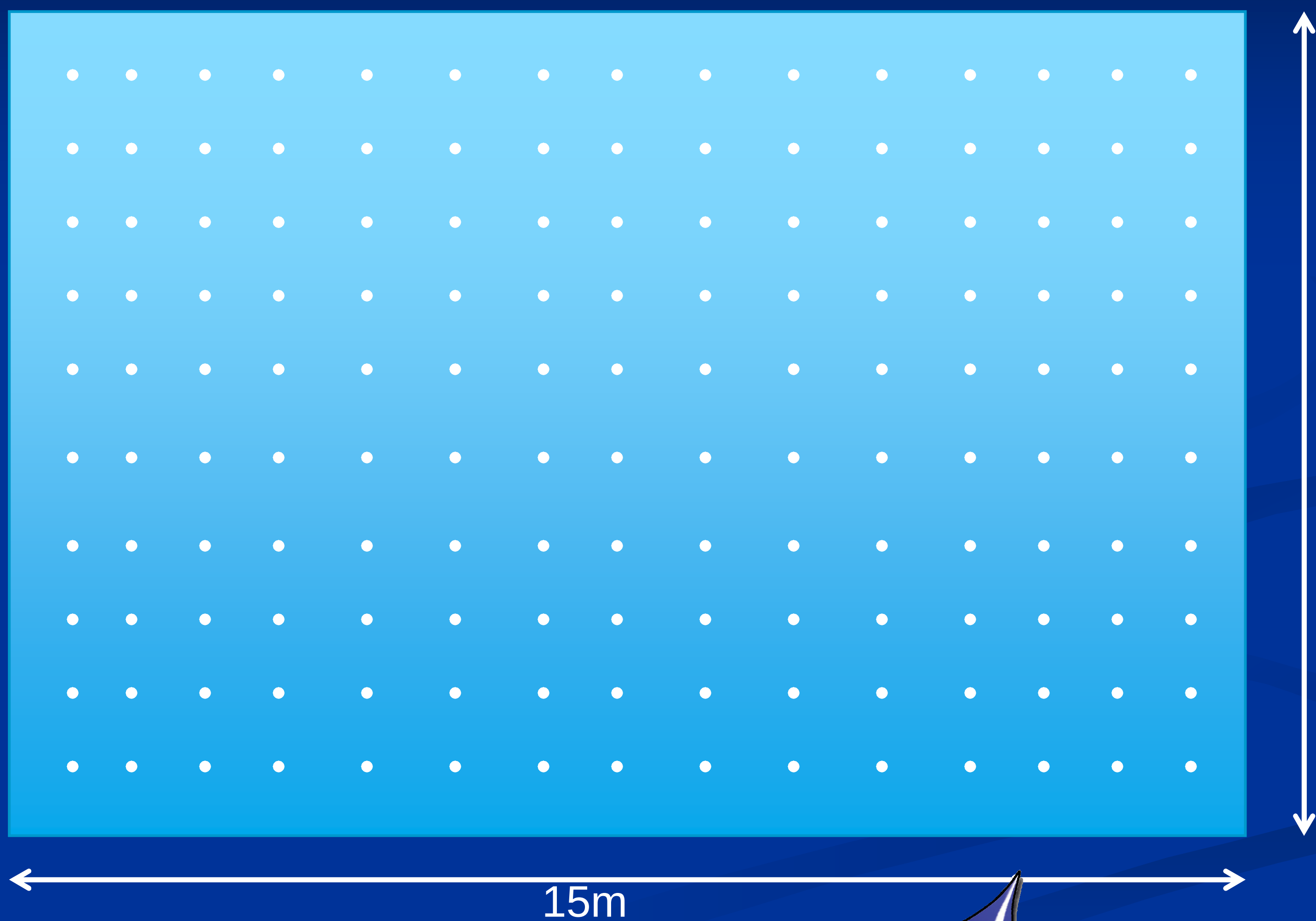
Mass ~ 720,000 kg
Pore volume ~ 112,500 L

Mass of contaminant for 10 mg/L
= 1.125 kg ~ 700 mL ~ 0.001% of pore volume

Note: More like 100 mg/L depicted in previous pore scale figures

Characterization Scale: Excessive?

150 soil samples, 5 cm diameter, 3 m long = 0.2% of total volume



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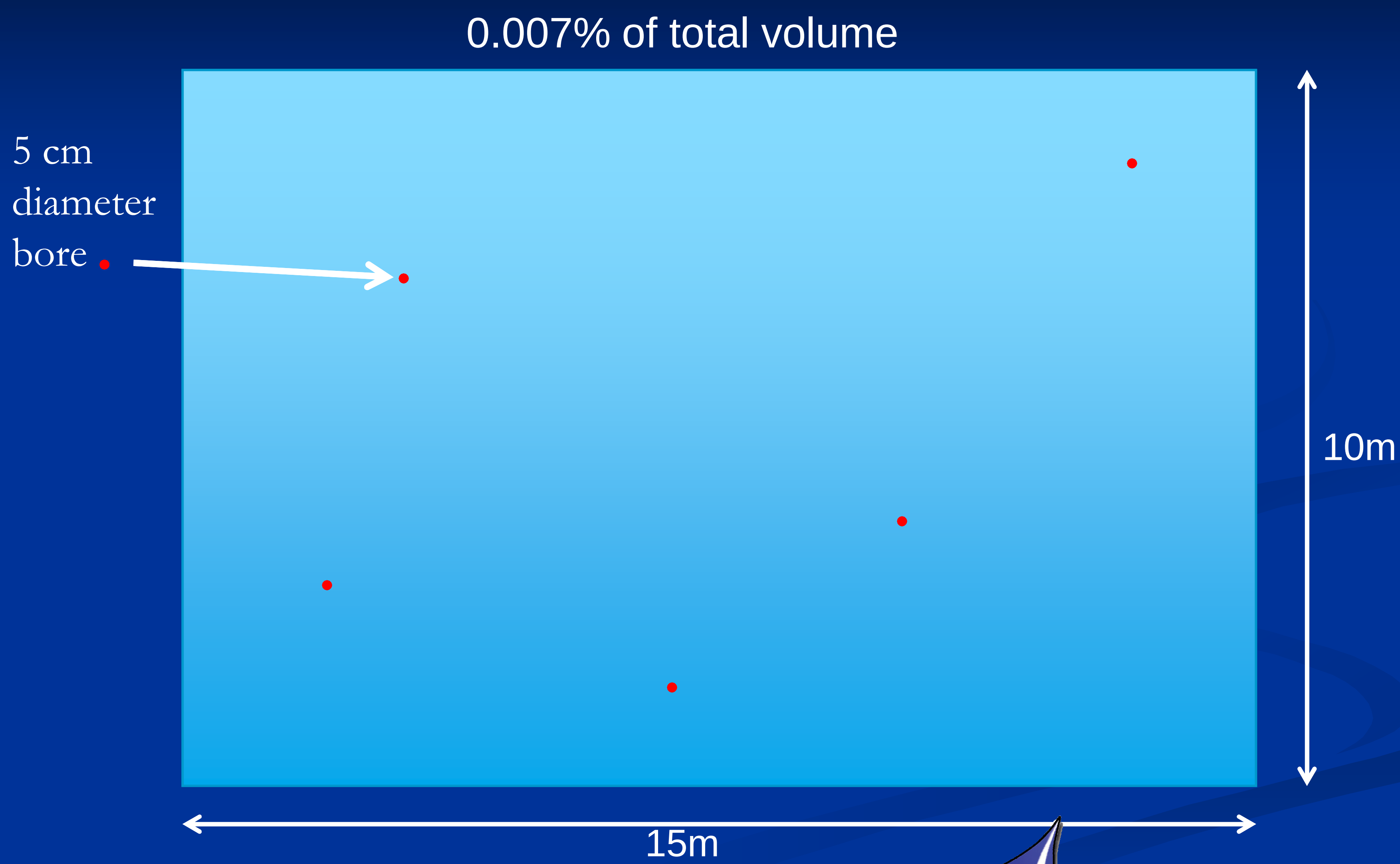
Characterization Scale: Reality



Remediation Approaches

Typically three types of approaches:

- Removal
- Immobilization
- Destruction

Removal Approach

- Contaminant Extraction (Liquid or Vapor Phase). Can also include:
  - Enhance permeability (e.g., frac)
  - Enhance solubility and mobility (e.g., heat, solvents, surfactants)
  - Enhance phase transfer or vapor pressure (e.g., heat, vapor pressure)

Immobilization Approach

- Isolate Source from Surroundings
  - Barrier Walls
  - In place encapsulation (cement, bentonite)
  - Change gradients or flow field (prevent movement)
  - Vitrification (solidify)
  - Change species/phase to reduce solubility or mobility (e.g., adjust pH, redox, etc.)

Destruction Approach

- **Chemically Transform Contaminant**
  - Chemical Oxidation
    (e.g., permanganate, persulfate, peroxide, ozone, etc.)
  - Chemical Reduction (e.g. ZVI)

- **Biodegradation**
  - Electron Donor/Acceptor and/or bacteria culture
  - Sufficient moisture to sustain cells

…Or a combination

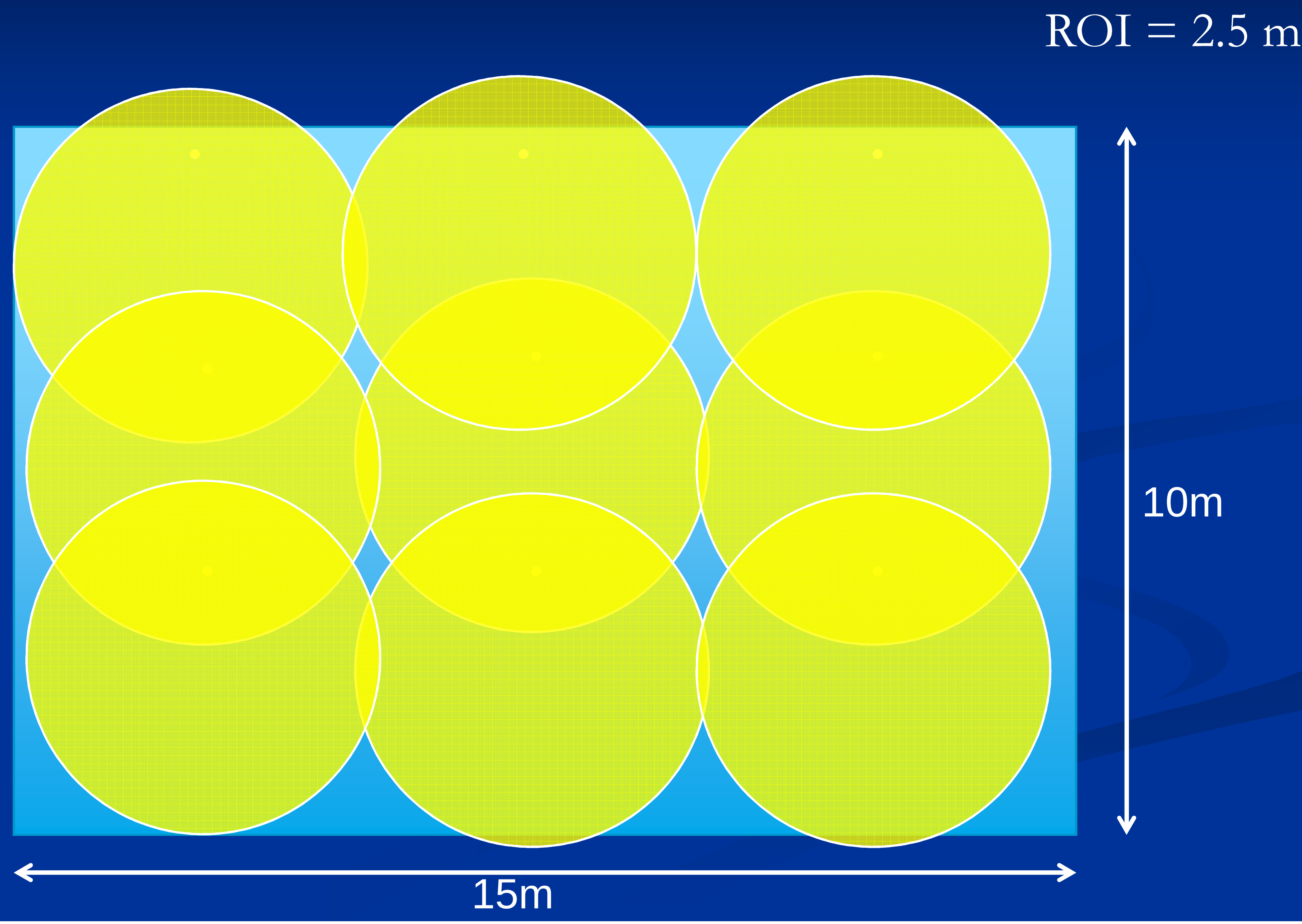
Causes of Failure - Contact

- Insufficient contact in active time period
  - Non intersecting pathways (e.g., zvi surface rxn)
  - Insufficient amendment/bacteria
  - Gas occlusion
  - Rebound from transport out of immobile zones

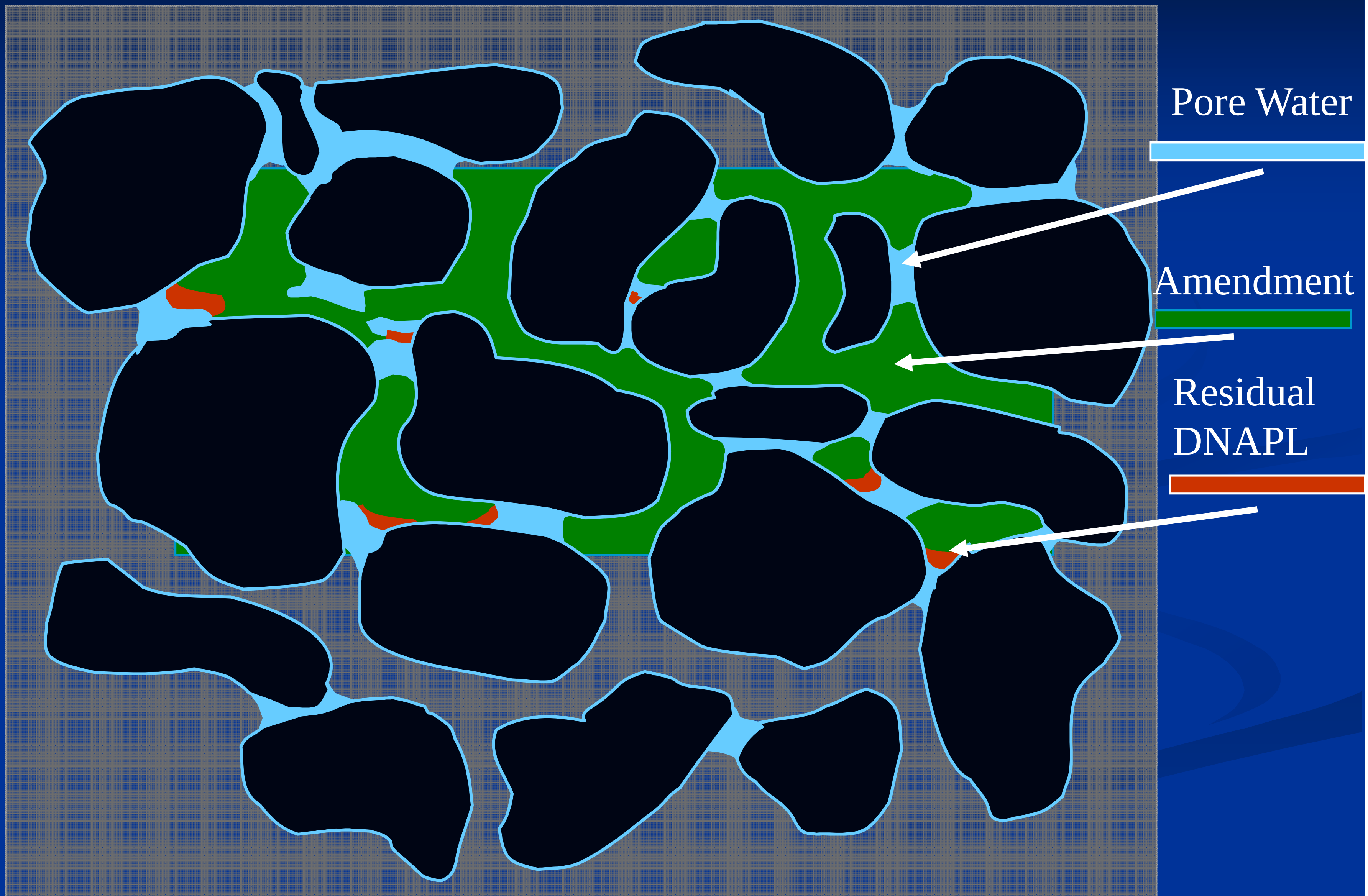
Causes of Failure - Chemistry

- Reaction and Stoichiometry
  - Low concentrations result in low kinetics
    - Purple doesn't necessarily mean threshold reached
  - Amendment depleted on non target compounds or species (e.g., reduced minerals, methanogens)
  - Redox/pH/supporting chemicals not satisfactory
    - Radicals (sulfate, hydroxyl) and persulfate rarely measured specifically
  - Not enough amendment

Remediation Scale: Injection Optimism in Plan View



Residual NAPL in Vadose Zone with Ideal Amendment Distribution



Injection Heterogeneity

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Injection Amendment Distribution

- Amendments typically applied and distributed non-homogeneously
- Often get lucky that amendments follow similar pathways to contaminant
- Enough amendment must be able to contact contaminants before being depleted by non-target compounds and, must remain in contact long enough for reaction to occur
- Injection is actually a non-contact sport

Injection Facts

- Will not fill the target pore volume, no matter how much you inject.
- Hope that injectate is following approximately the same permeability opportunities that contaminant has (advection and diffusion).
- Increase odds with multiple points

Issues Complicating Injection

- Daylighting increases w/volume and near surface
- Sometimes displace fluids (but rarely add contaminants)
- Consider permeability issues created by reaction such as heat, gas or precipitated solids
  - Heat can create pressure that will move fluids away
  - Gas (O_2, CO_2, CH_4, H_2, H_2S) can occlude pores, reduce flow
  - Solids (MnO_2 or Fe oxides) can occlude pores, or sorb chemicals

Soil Blending

- Improves distribution by diminishing constraints of permeable pathways
- Increases homogeneity of heterogeneous system
- Apply amendment while mixing, better distribution
- Never 100% homogenized, but much better than 2D injections (really 1D*X)
- May need to re-establish soil cohesive strength

Soil Blenders and Augers

- **Large diameter augers -** great for deep applications at well characterized sites, not as efficient for large areas.
- **Soil Blenders** are limited in depth (~ 22') without benching but:
  - Can efficiently blend large areas
  - Construction rates 200 to 600 tons per day
  - Fit on standard size equipment (e.g., excavator) so smaller equipment footprint
  - Lower mob/demob costs

BECAUSE NOT ALL *IN SITU* SOIL BLENDERS ARE CREATED EQUALLY

ALLU	REDOX-LANG	REDOX TECH
		
PMX-500 Working Depth: 16.4 feet Constant Power: 90 HP Dual Motors: Yes Automatic Power Control: No Reach Working Depth in Clay: No Blend Weathered Rock: No	**Modified Lang** Working Depth: 25 feet (with extension) Constant Power: 200 HP Dual Motors: No Automatic Power Control: No Reach Depth in Clay: Sometimes Blend Weathered Rock: Maybe	**Redox Tech Custom** Working Depth: 20 feet Constant Power: 376 HP Dual Motors: Yes Automatic Power Control: Yes Reach Working Depth in Clay: Yes Blend Weathered Rock: Yes

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Soil Blender Performance

- Can blend soil in situ to 22’ below grade
- 21,000 ft-lbs of torque at head allows dry and wet mixing
- **Can efficiently blend to depth with head completely submerged**.
- Cheese Analogy for remediation contact
  - Injection – Blue or Stilton
  - Weak blend – Cottage
  - Strong blend - Ricotta

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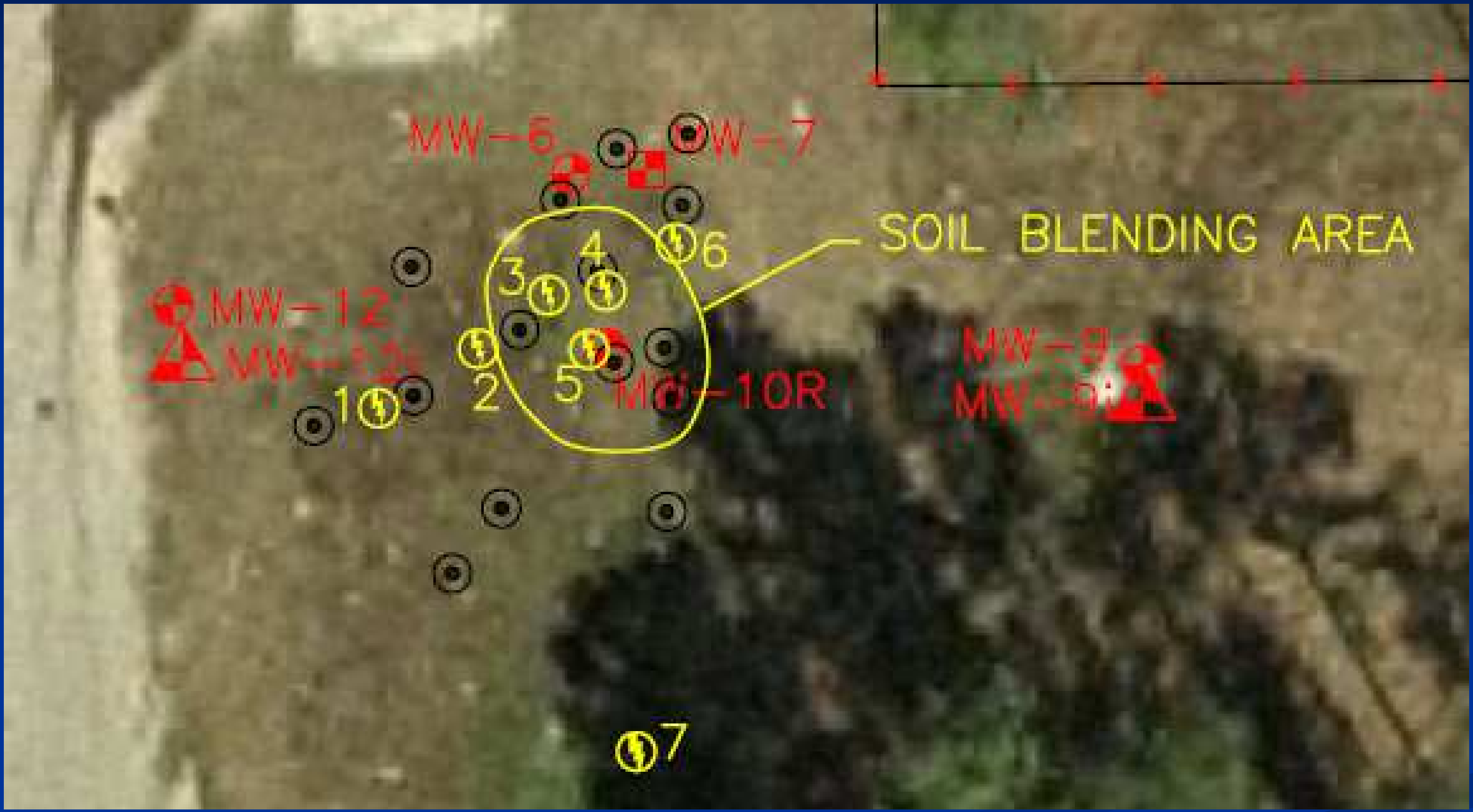
Injection vs Soil Blend



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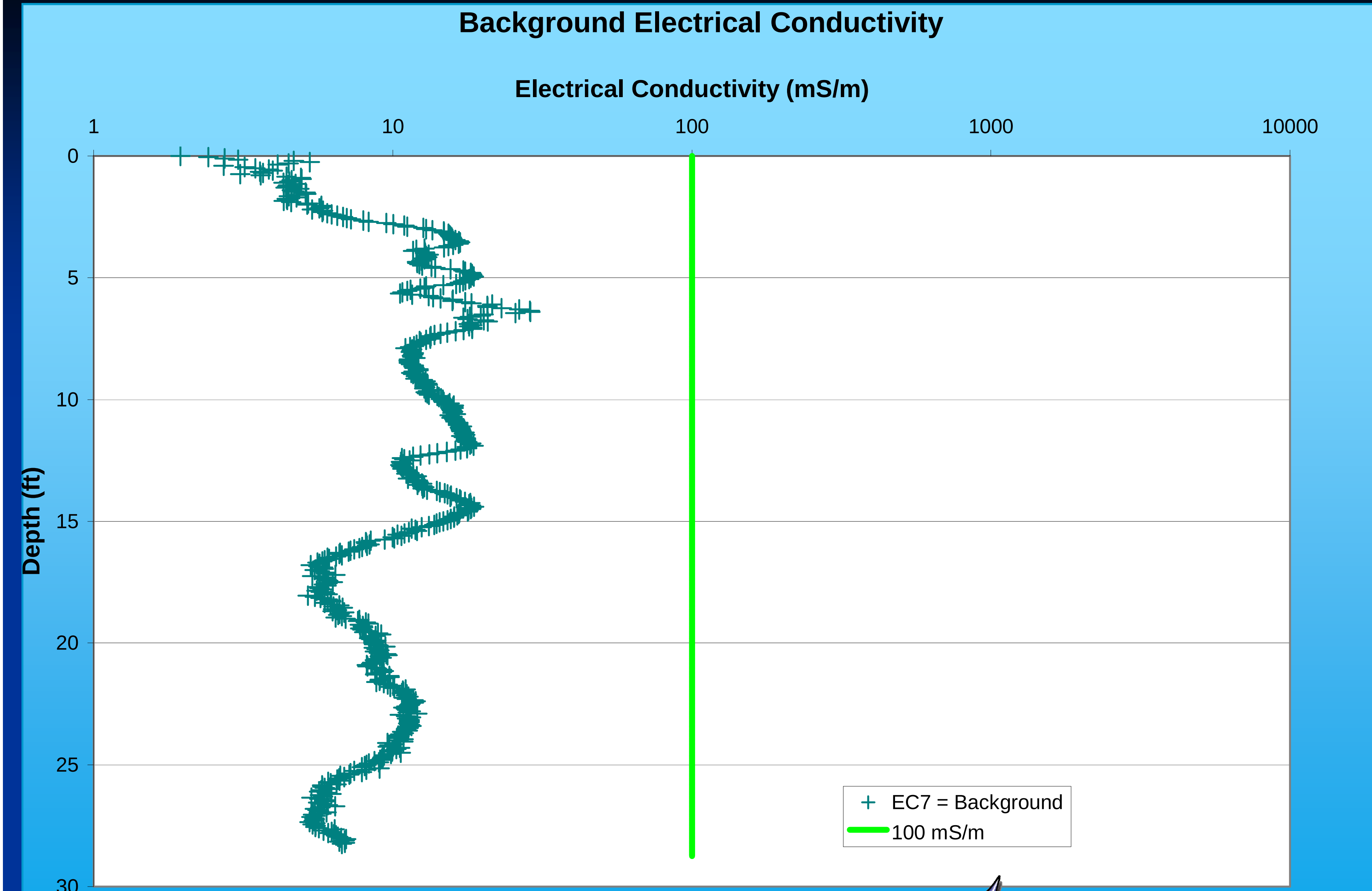

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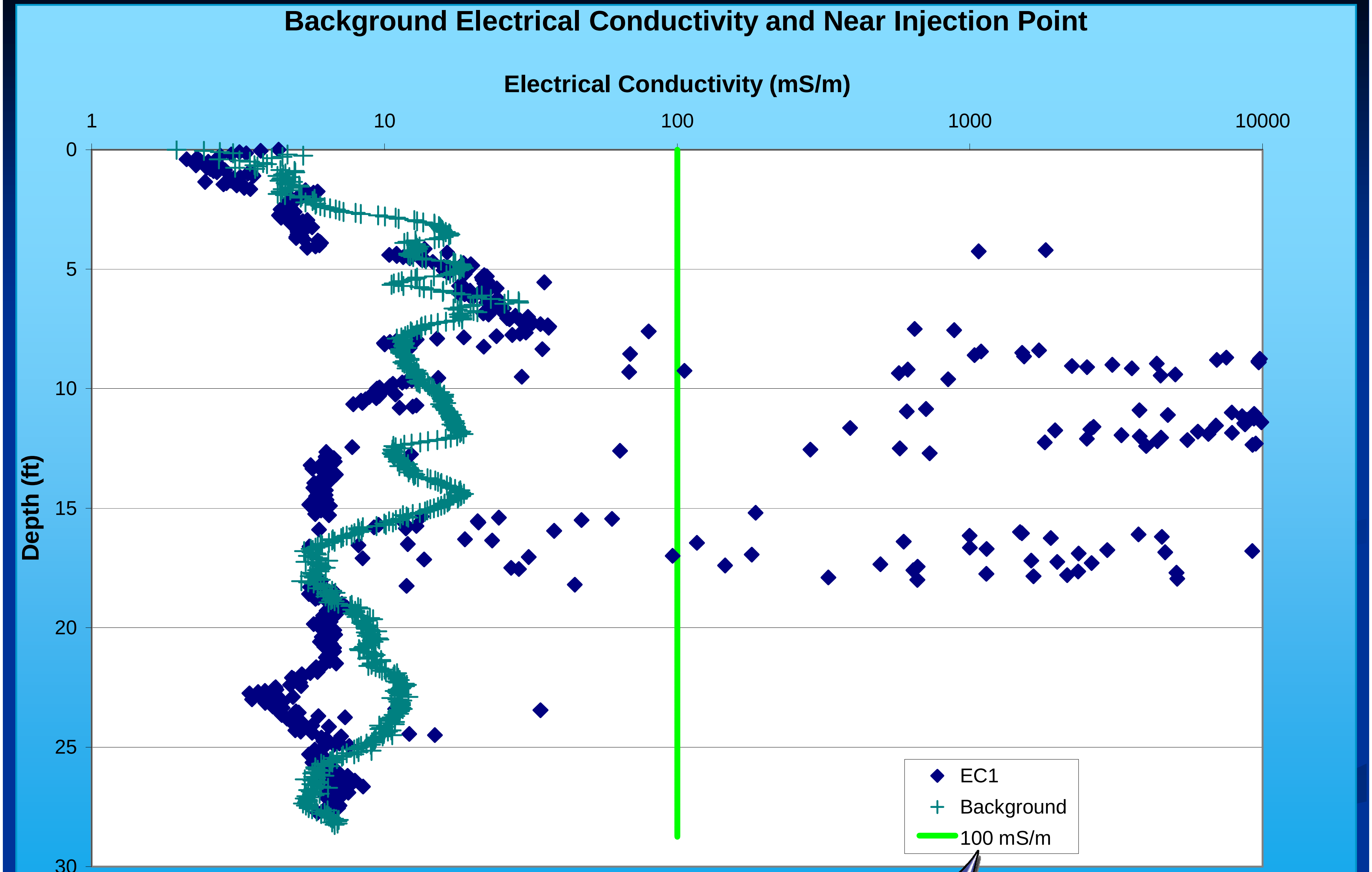

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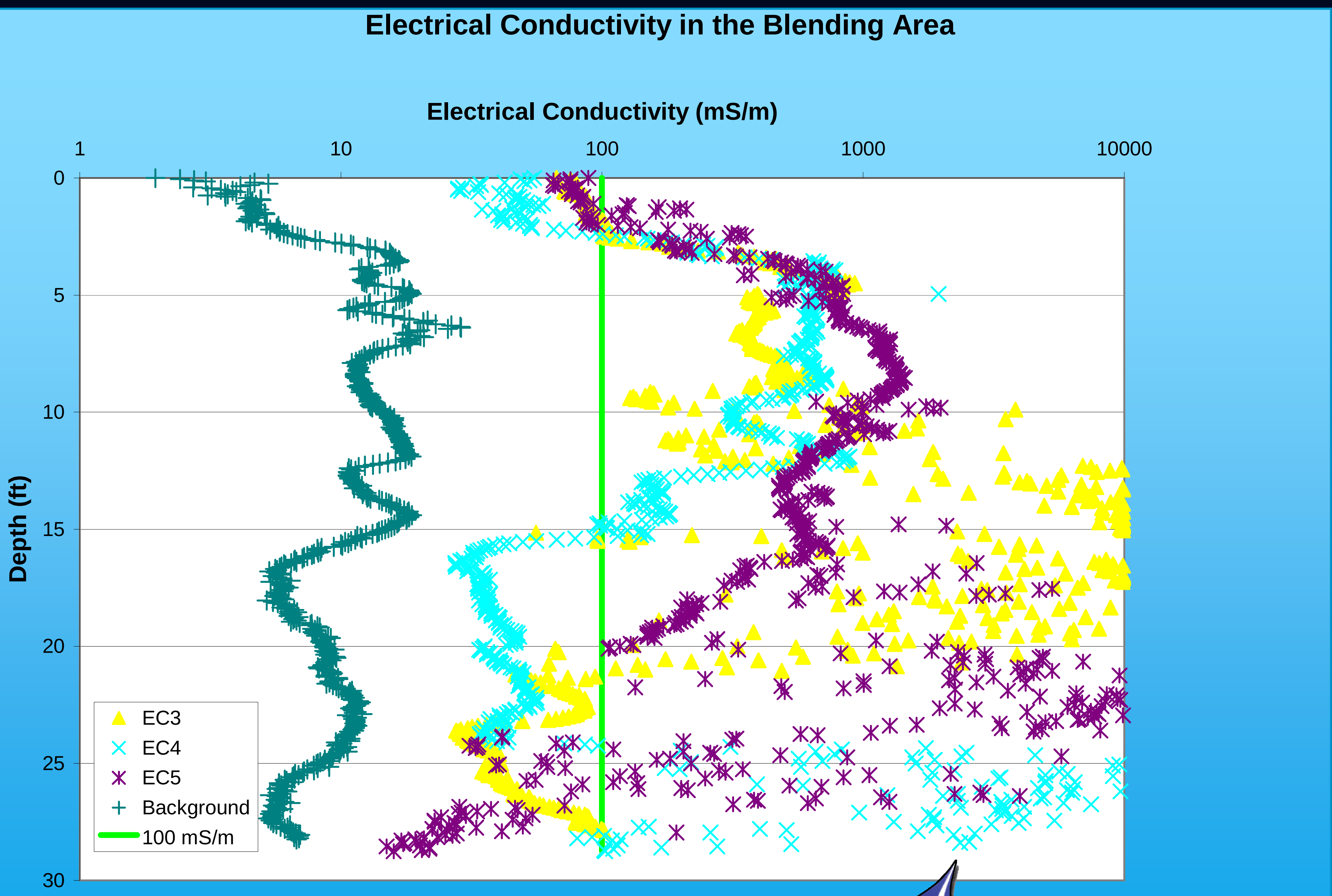

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Hygroscopic amendments aid vadose zone remediation

- Maintain enough fluid for transport of amendments or cells to contaminant (or vice versa)
- Enough fluid to support growth of cells
  - Microzone research suggests less needed than previously thought
- Other Properties of Amendments
  - consume-able; reduce contaminant flux; suspend solids; thixotropic
- Examples: sugars, salts, alcohols, guar, silica flour, bentonite

Case Study #1 – Coastal Plain Vadose Zone

- Dry cleaner Site in North Carolina
- Vadose Zone application from 4 to 8 feet bgs (500 sq ft)
- PCE in Soil (sand, silt, clay)
- Test of several amendments including oxidants and bioenhancements
- Concern about biodegradation in unsaturated zone

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Case Study #1 – Pilot Test

- 5 Test Cells
  - Control (dry blend) 5’ x 5’ x 7’
  - Chitorem 10’ x 10’ x 7’
  - Crab shell 10’ x 10’ x 7’
  - ABC+ 15’ x 15’ x 7’
  - Hydrogen peroxide, then Kperm 15’ x 15’ x 7’
- Multiple soil samples from each cell five times over 5 months,

Case Study #1 – Pilot Test Results

	Control Dry Mix	Chitorem	Crab shell	ABC^+	H2O2 then Kperm
Pre PCE (mg/kg)	6.425	0.782	0.032	11.629	2.383
Post PCE (mg/kg)	1.365 79%	0.162 79%	0.076	0.008 99.9%	0.258 89%

- High ethene, ethane in ABC^+ (> 4 orders)
- High methane in crab shells (> 2 orders)
- DHC in Chitorem and crab shells

Case Study #1 – Full Scale Blend

- NC Coastal Plain Blend (~222,000 cu ft = 12,210 tons) 16 days
- Pre-blend water saturation = 0.69 (avg. porosity = 0.39)
- ABC^+ blended in at 1.25 wt% in target areas

Case Study #1 – Full Scale Blend Results

Avg Concentrations (mg/kg)

	Pre Blend	Post (3 months)	Post (8 months)
PCE	4.001	0.157	0.125 96%
TCE	0.189	0.013	0.007 96%
cDCE	0.057	0.826	0.043 25%
VC	ND	0.079	ND

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Case Study #1 – Conclusions

- Reductive dechlorination will work in vadose zone (often already working)
- Likely dependent on moisture content/contiguity and persistence
- Residual volatile contaminants often higher in higher moisture content areas (finer grain, lower permeability), so vadose zone success is not surprising
- Cost of project $234,000 ($29/cu yd or $20/ton)

Case Study #2

- Industrial Site in Ohio
- Site soil consisted of silt and clay
- TCE in Soil as high as 63,000 mg/kg
- Years of active SVE was ineffective
- ISCO with In Situ Soil Blending selected as best approach

Case Study #2

- 4,658 square feet from ground surface to 20 ft bgs over 10 day period
- 78,662 lbs of potassium permanganate (based on stoichiometric demand and background soil oxidant demand)
- During soil blending the SVE system was removed
- Project completed for $286,700 (~$91/cu yd or $61/ton)

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Case Study #2

- 41 post blending soil samples were collected

	Pre Treatment (mg/kg)		Post Treatment (mg/kg)		Remedial Goal (mg/kg)
	Maximum	Average	Maximum	Average	
Area A	4,200	226	390	265	1,948
Area B	583	155	380	121	
Area C	63,000	902	1,300	302	

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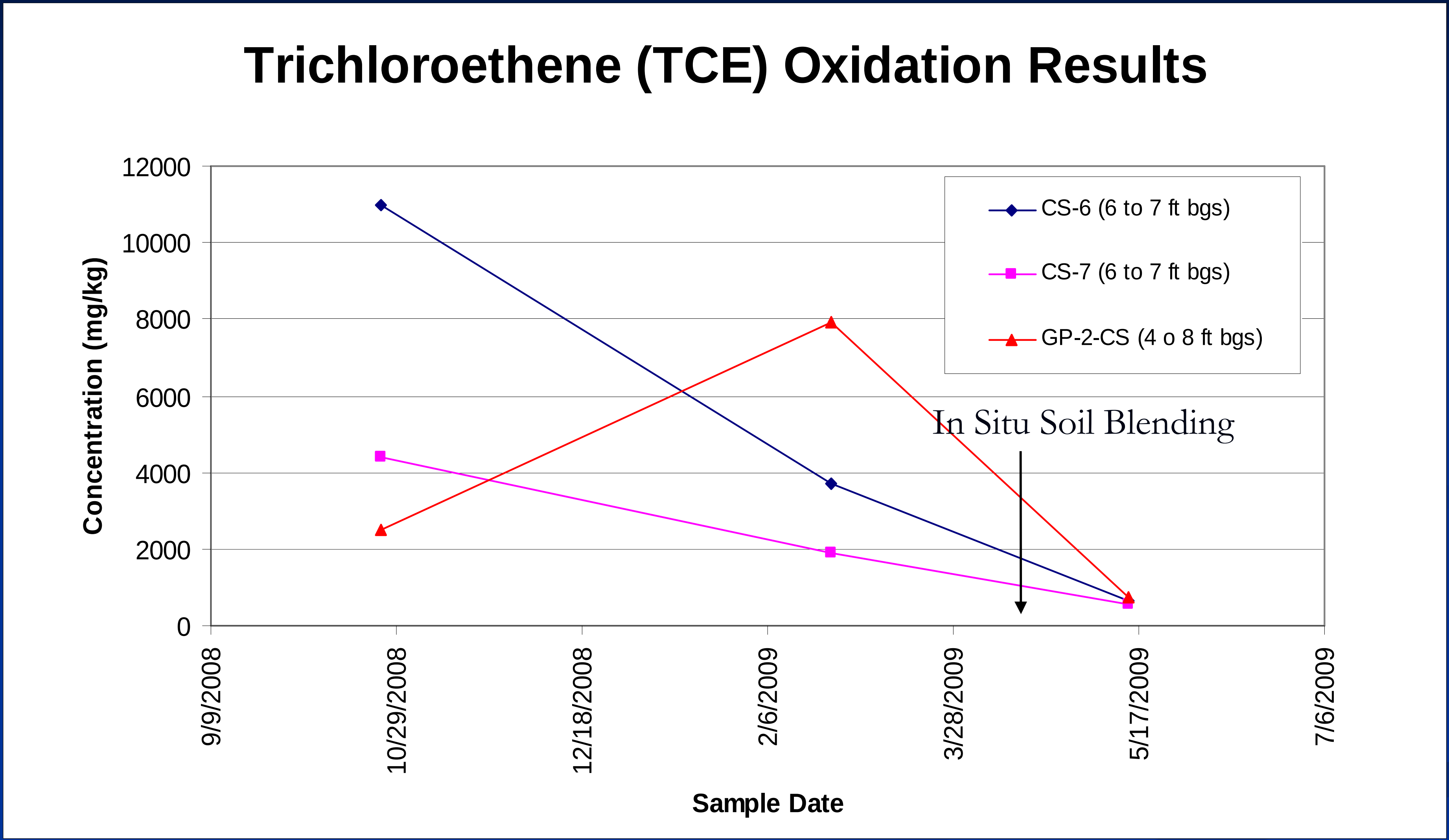
Case Study #3

- Industrial Site in Illinois
- Vadose Zone application in clays and silts from 4 to 8 feet bgs (500 sq ft)
- TCE in Soil as high as 10,000 mg/kg
- Prior mixing using a conventional backhoe with a peroxygen ineffective at achieving remedial target (1,300 mg/kg = soil saturation limit)
- Soil concentrations remained at 7,000 mg/kg

Case Study #3

- In Situ Soil Blending with Potassium Permanganate selected
- Applied 2,670 lbs of Potassium Permanganate
- Work completed in one day for $17,500 (~$233 cu yd or $155/ton)

Case Study #3



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Remediation Cost

- Injection is inexpensive but limited distribution
  - Typically \$10 to \$50 per ton (min \$250,000 per acre)
- Blending is relatively inexpensive (\$15 - \$20 per ton)
- Amendments range from inexpensive (\$5 per ton bulk soil) to expensive (\$60 per ton bulk soil)
- Excavation and removal can be expensive
  - Tipping cost can range from \$10 to >\$100 per ton
  - Transportation cost > \$0.05/ton x number miles

Petroleum Exploration Challenges

- Oil and Gas Production derived waste
- Brine, organics, fracking fluids
- Stored in lined or unlined waste pits
- Oxidation, reduction, pH adjustment, stabilization, solidification

Summary

- Better Access to contamination results in better remediation
- Blending can provide better Access than injection
- Amendment-based remediation in the vadose zone can be successful with blending and proper amendments

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