Lessons Learned and Paths to Success with Activated Carbon Injections

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Various sources as cited

What we’ll cover today:

1. High Resolution Site Characterization (mass identification)
2. Properties of Activated Carbon (scientific justification)
3. How AC-based Amendments Work
4. Methods of Application
5. How Much to Inject? (dosing)
6. Injection and Process Issues
7. Recommendations
8. Questions/Discussion

Success Reported for BOS-200 in KY

- High pressure injection required to cope with low permeability geology.
- Emphasizes the importance of building high resolution CSM for remedial design and implementation to be effective.
- Out of 72 UST sites in total:

  41 NFA (10% 2nd injection selected)

  7 requested NFA,

  24 in monitoring stage

  (19/24 are less than 1 year post injection)

CBI in Colorado

- Over 225 facilities treated since 2005.
- Usually tried when other methods unsuccessful / impractical.
- Significant reductions (>90%) in dissolved BTEX noted.
- Visible carbon usually in wells.
- Rebound and/or additional treatment often occurred.
- About 15% of sites treated with CBI reached NFA.
  - Small areas (<1000 ft^2)
  - Low concentrations (<700 ug/L benzene (usually <200))

Sampling Uncertainties (examples)

- Field:
  - ➢Sample location bias
  - ➢Sample collection bias
  - ➢Sample preservation
  - ➢Number of samples (over time, by volume)
- Geological:
  - ➢Internal bias due to soil type
- Analytical:
  - ➢Sample selection from container by lab?
  - ➢Dubious field measurements

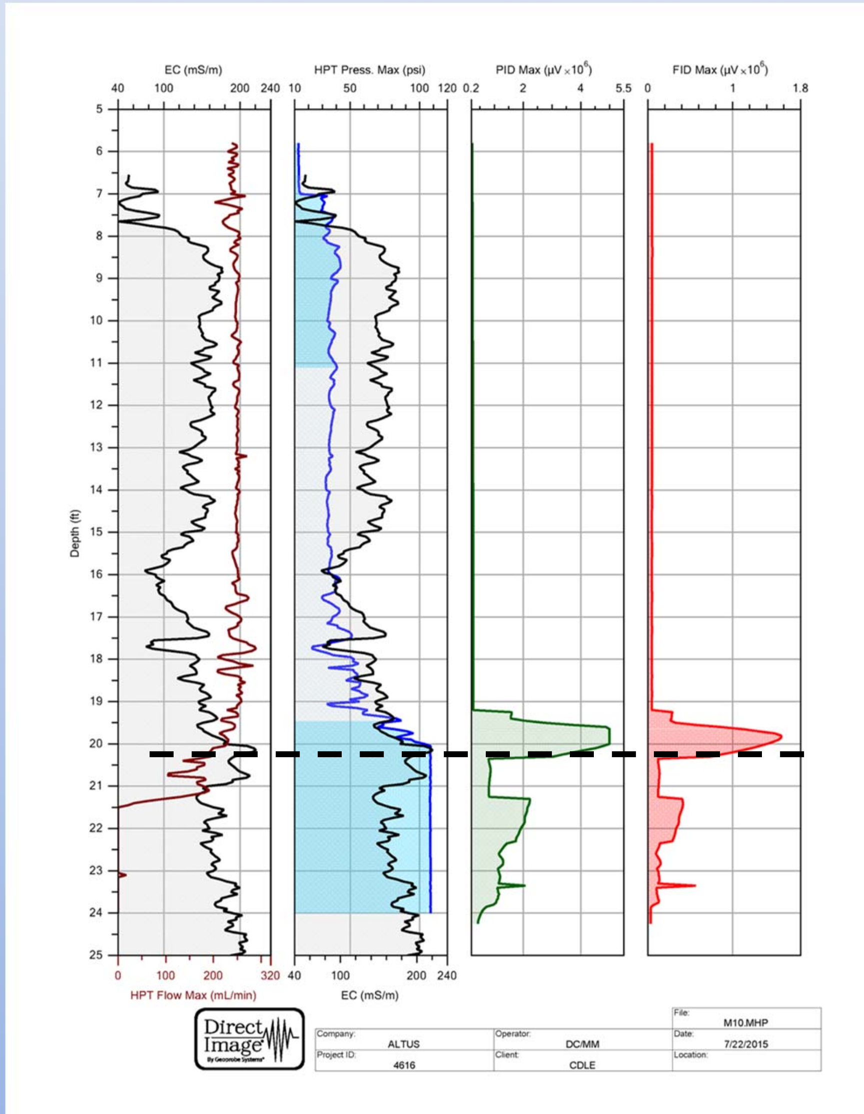
PRECISION IS LACKING

1. High Resolution Site Characterization (HRSC)

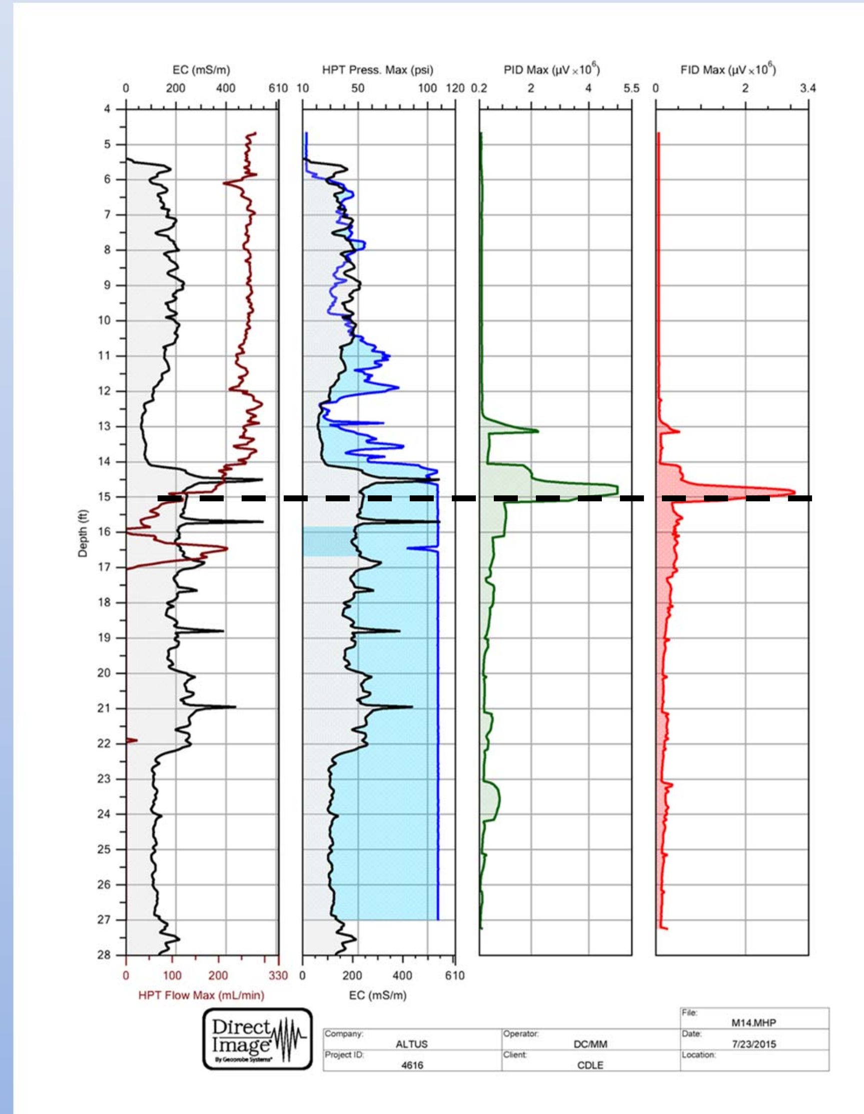
- Purpose:
  - ➢ Refine the Conceptual Site Model (CSM)
  - ➢ Better estimate hydrocarbon mass
- Methods:
  - ➢ MIP/LIF/HPT
  - ➢ Direct push/continuous core/lab samples
  - ➢ Geophysics (surface and downhole)
- Interpretation
  - ➢ Understand the tools/results
  - ➢ What should you get from your contractor?

"Remediation under-performance or failure is due to a lack of understanding of site conditions and transportation/degradation processes "

MIP output



EC (mS/m)
HPT Press. Max (psi)
PID Max (µV x 10^6)
FID Max (µV x 10^6)
Depth (ft)
HPT Flow Max (mL/min)
EC (mS/m)
Direct Image
Company: ALTUS
Project ID: 4616
Operator: DC/MM
Client: CDLE
File: M10.MHP
Date: 7/22/2015
Location:



EC (mS/m)
HPT Press. Max (psi)
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Depth (ft)
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Direct Image
Company: ALTUS
Project ID: 4616
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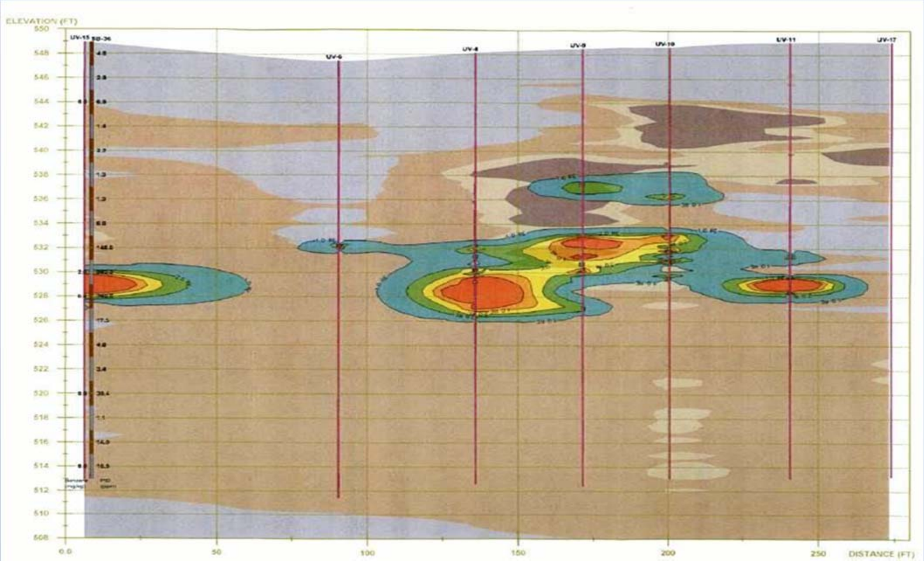
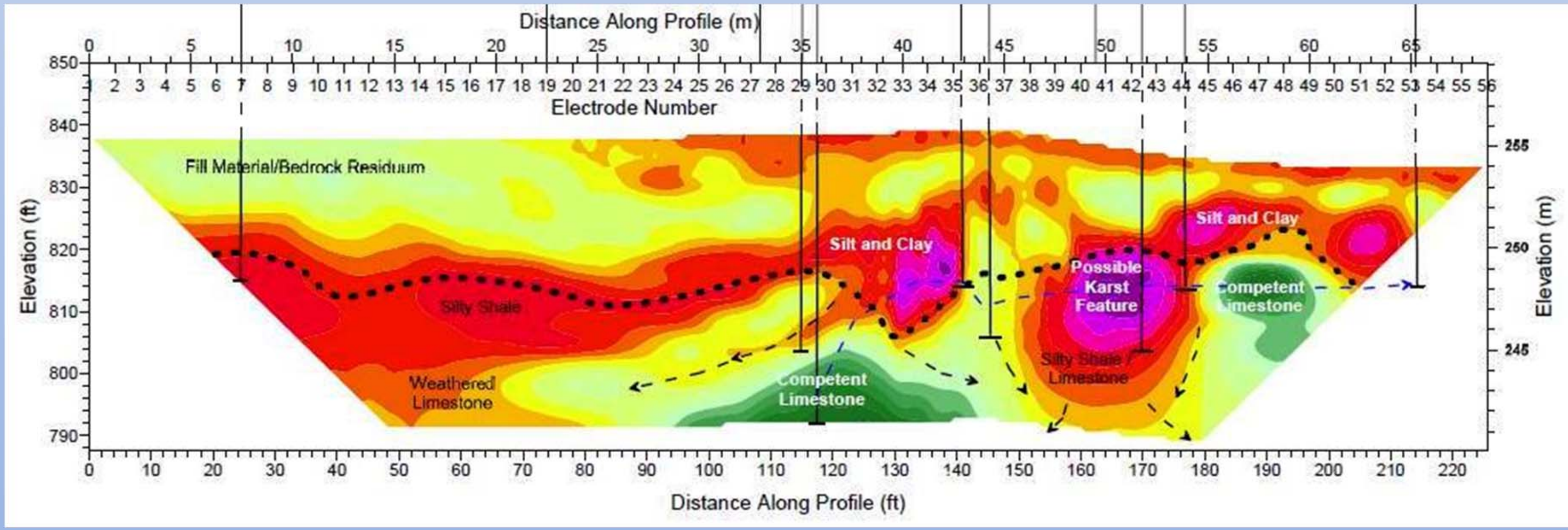
Client: CDLE
File: M14.MHP
Date: 7/23/2015
Location:

High Resolution Geophysical Tools

Downhole Geophysical Logging



Surface Geophysical Methods 2D



2. Properties of Activated Carbon

✓ Sources and activation process

✓ Surface area/particle sizing

✓ Pore sizes/structure (adsorption)

Sources

- Bituminous Coal
- Coconut Shell
- Sub-Bituminous
- Lignite
- Peat
- Wood
- Petroleum
- Bone Char

- ➢ Each type of material will have different porosity distribution and surface area when activated.
- ➢ The most popular carbon used for liquid-phase slurry injection is bituminous coal-based because of its hardness, abrasion resistance, pore distribution, low ash content and low cost.

Activation Process

- Chemical (1900) - heating of the carbonaceous material in the presence of dehydrating chemicals such as zinc chloride or phosphoric acid
- Steam (1901) – heating with steam and carbon dioxide (anoxic)

➢ Longer activation times result in larger pore sizes.

➢ Preferable to use virgin and not regenerated carbon (latter may have residual impurities)

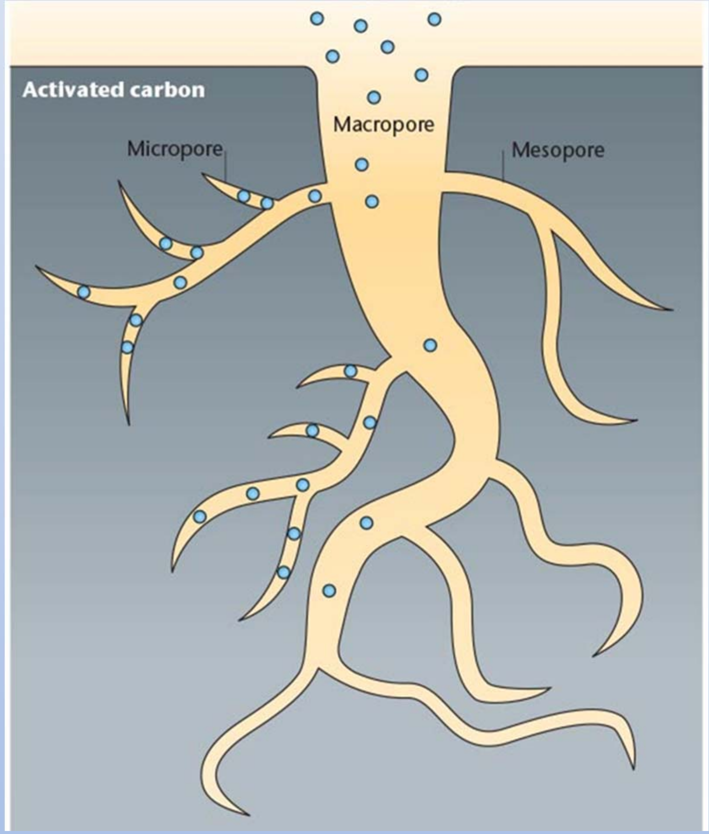
Envirocarbon.com

Pore Sizes

- **Transport pores** are >5 molecular diameters to visible cracks and crevices. Transport pores are too large to adsorb and act simply as diffusion paths to transport the adsorbate to the adsorption sites.
  - Macropores (>50 nm diameter) (=.05 µ)
  - Mesopores (2-50 nm diameter)

- **Adsorption pores** are the smallest pores within the particle, consisting of gaps between the graphite plates. 40% of the carbon particle/granule volume
  - Micropores (< 2 nm diameter) (=.002 µ)

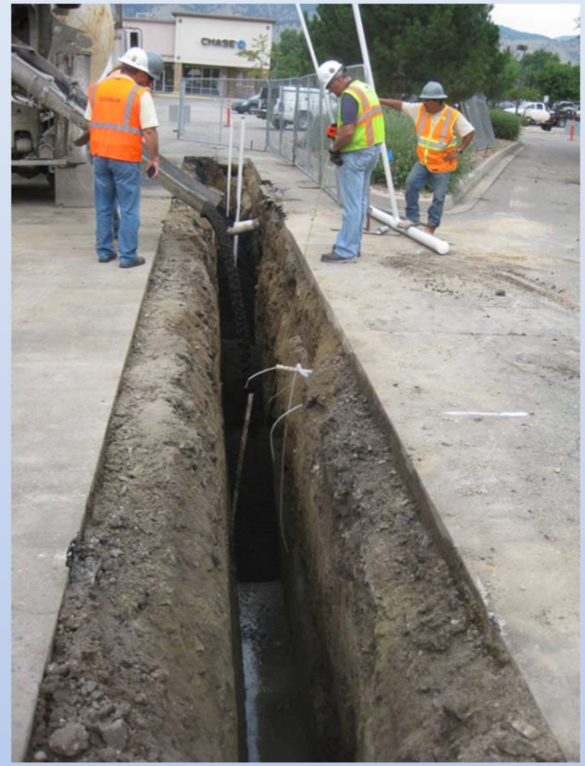
Macro and mesopores are the highways into the carbon particle while micropores are the parking lots.



Pore size: IUPAC system (International Union of Pure and Applied Chemistry):

Grind / Surface area

Cocarb.com



Activated carbon

Granular Large internal surface area and small pores

1. Total surface area 500 and 2000 m^2/g
2. Micropore surface area 175 to 650 m^2/g
3. Micropore volumes 0.15 to 0.70 cm^2/g

Powdered Small internal surface area and large pores

Grind / Surface area

GAC vs. PAC? ---------------

: GAC has >90% retained by an 80-mesh sieve (177 µ) [ASTM D2862]

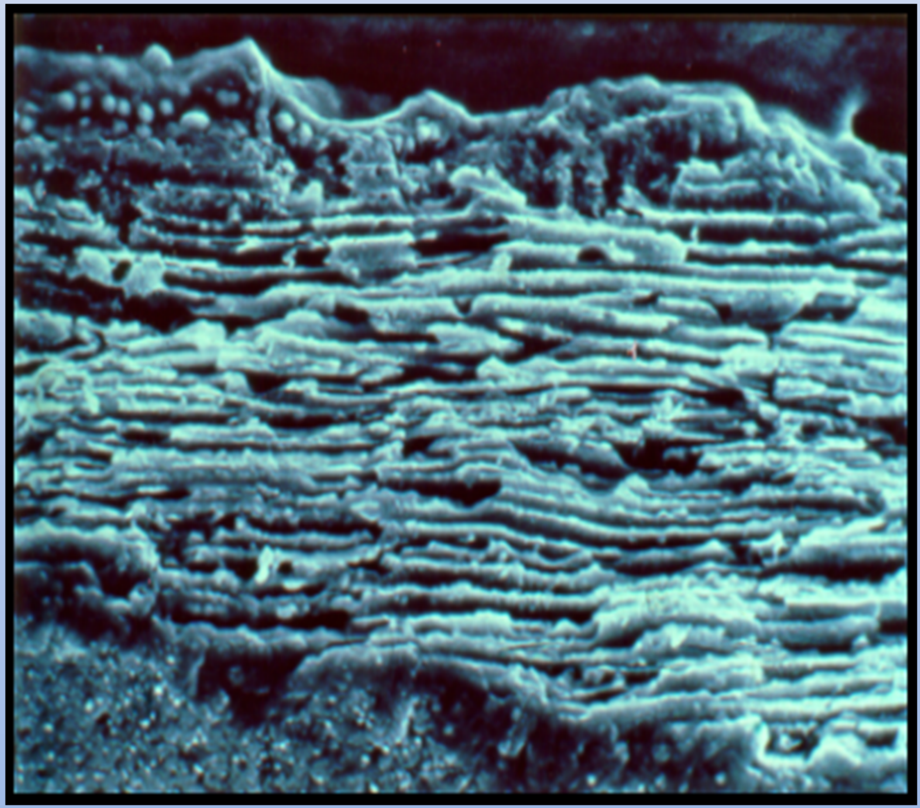
: *>4x larger than PAC*

5 grams of carbon has a surface area equivalent to a professional football field - including the end zones! (5348 m^2)

Iodine values from 450 to 1100 mg/g are typical and it is used as a measure of micropores.

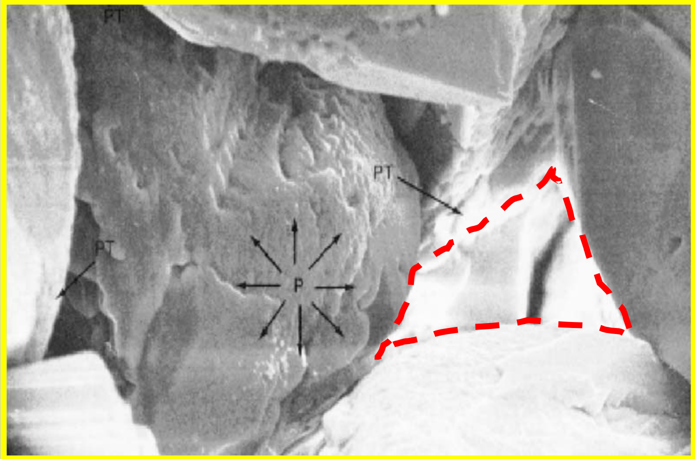
HIGHER VALUES ARE GENERALLY BETTER

Sorption driven by diffusion (concentration gradient) and Van der Waals forces



Powdered Activated Carbon (PAC)

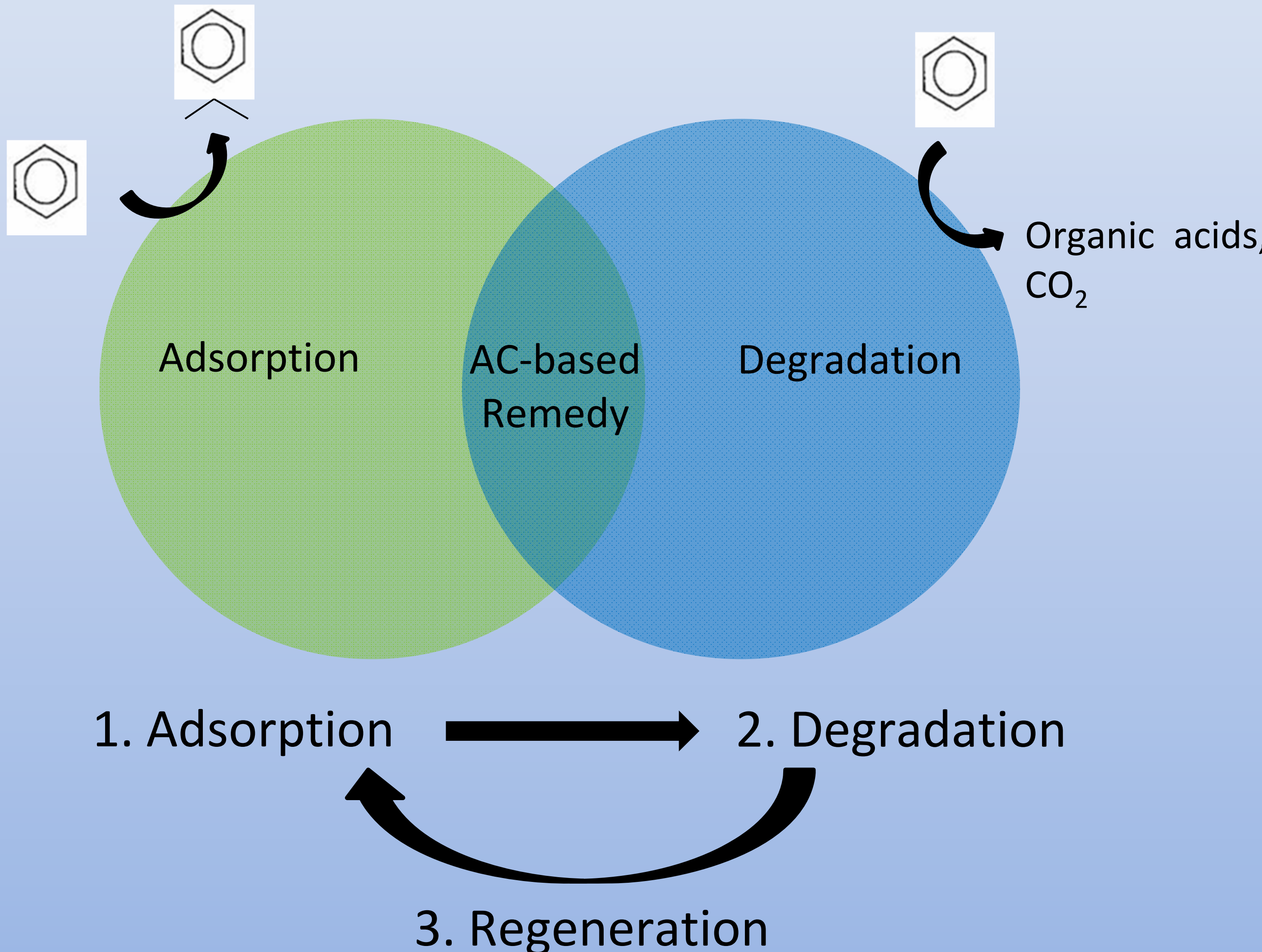
Particle size <40 microns (µ)



- ➢10-slot screen = 256 µ
- ➢200-mesh sieve (clay) = 75 µ
- ➢Bacteria = 0.5 - 2 µ
- ➢Pore throats (*Nelson, AAPG Bull., 3/09*):

  sand >2 µ *silt* 0.03 – 2 µ *clay* 0.005 – 0.1 µ
- ➢Mesopore = 0.05 µ; Micropore = 0.002 µ
- ➢BTEX molecules = 7 Angstroms (Å) = 0.0007 µ
- ➢Water molecule = 3 Angstroms (Å) = 0.0003 µ

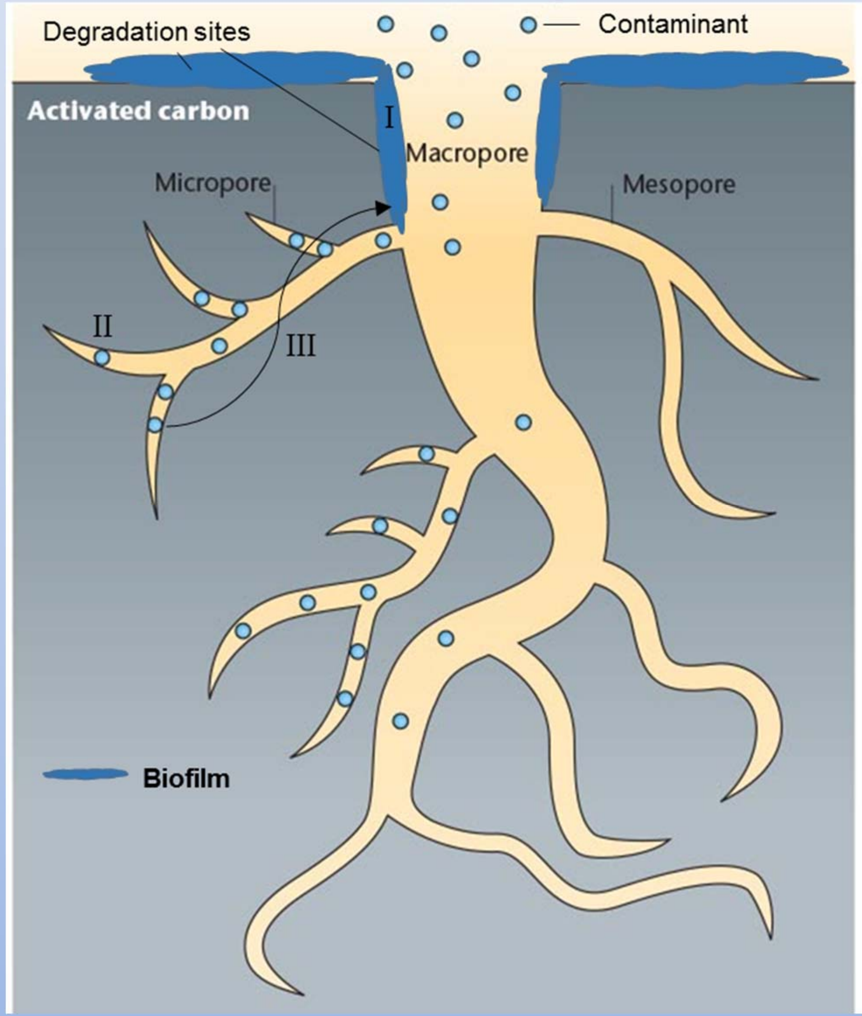
3. How AC-based Amendments Work



Advantages Claimed

- FAST RESPONSE (due to adsorption)
  - Weeks to Months
- NO REBOUND
  - Sustained treatment: regeneration counters back diffusion from soil
  - Limited number of injections needed

Degradation: Conceptual Model



Two Step Process

- Adsorption dominant before biofilm is established (Process II)
- Biodegradation dominant once biofilm is established (Process I)
- Remaining adsorption capacity is not used during steady state but mainly serves as emergency capacity:
  - Higher influent conc.
  - Decreasing biodegradation rate

Two Biological Approaches

Aerobic

- Present in Subsurface
- Hydrocarbon Degraders
- Well Understood Biology
- High Degradation Rates
- High Growth Rate
- Indigenous Microbes

Facultative Anaerobes

- Present in Subsurface
- Hydrocarbon Degraders
- Less Understood Biology
- Lower Degradation Rates
- Low Growth Rate
- Added Microbes
- In Fine Grain Soils or at Depth: Easier to Maintain Anaerobic Environment

Indications of biological activity

1. Nitrates drop almost immediately (< month)

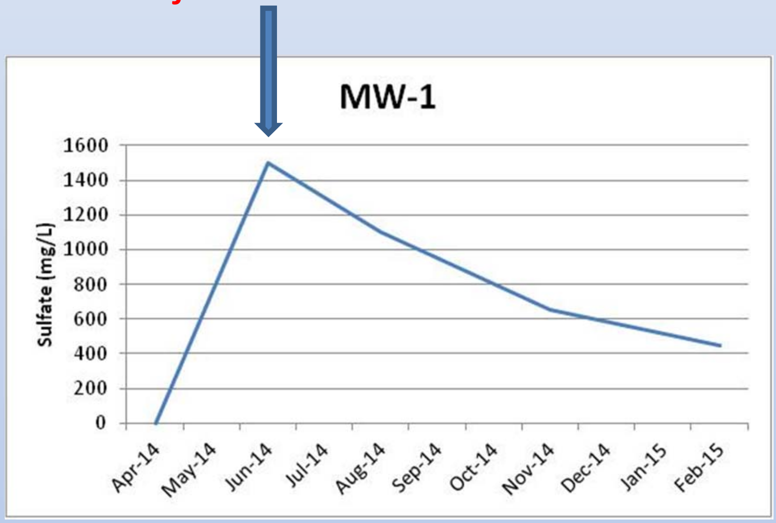
2. Sulfates drop over time (≈20% of wells may not drop)

3. Dissolved oxygen generally decreases

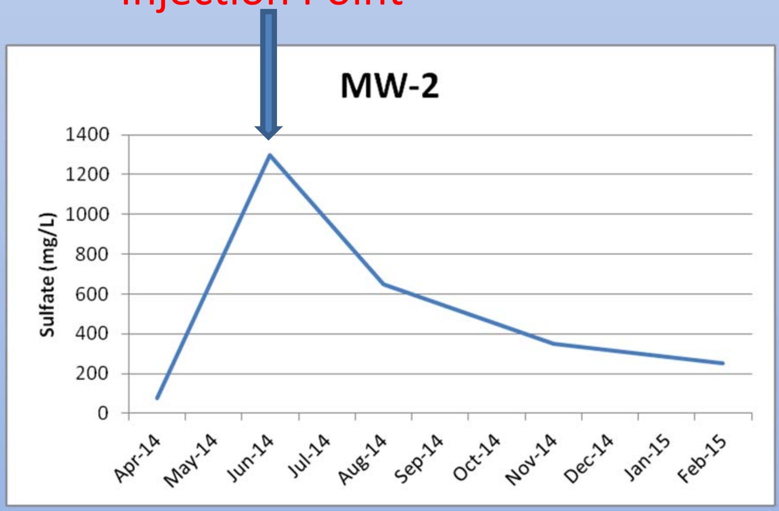
4. Oxidation Reduction Potential (ORP) stays generally negative.

Note: ORP does not characterize the capacity to acquire electrons and be reduced. It is a measure of intensity.

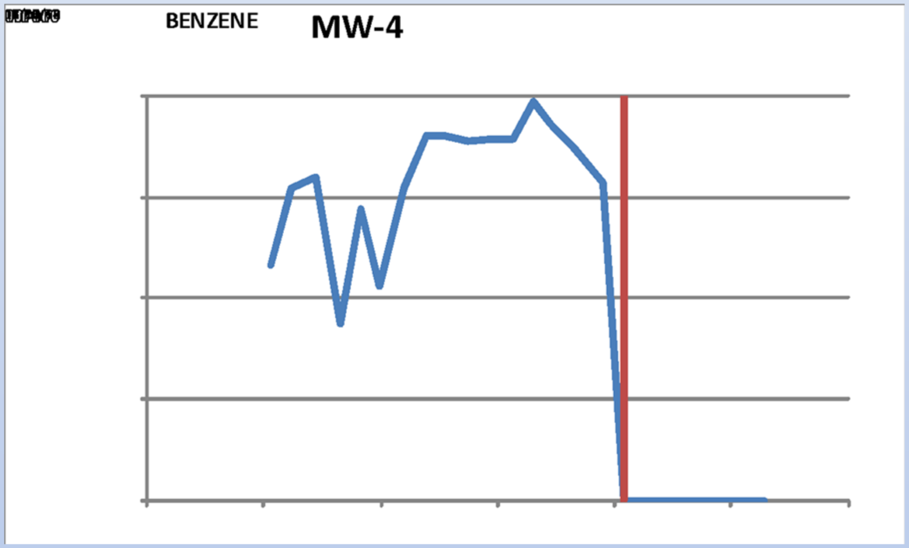
Injection Point



Injection Point

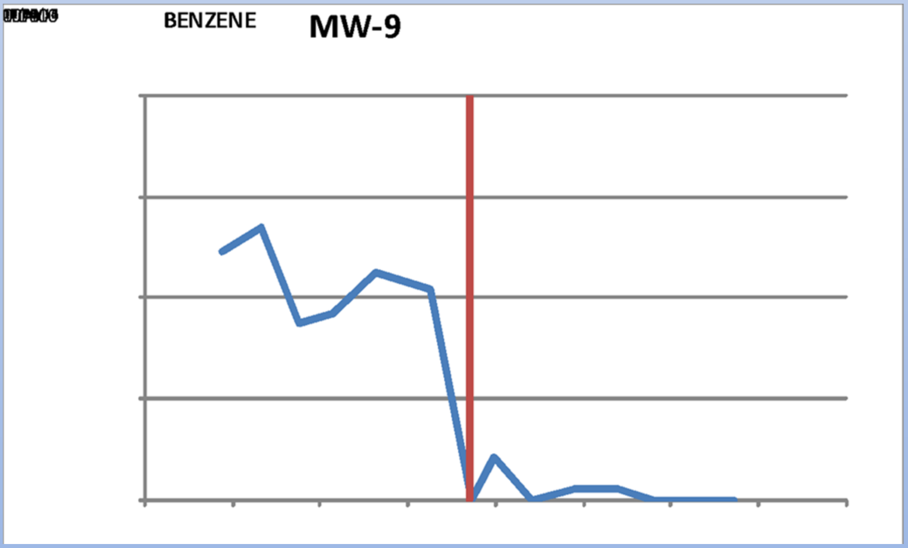


Typical well responses after CBI:



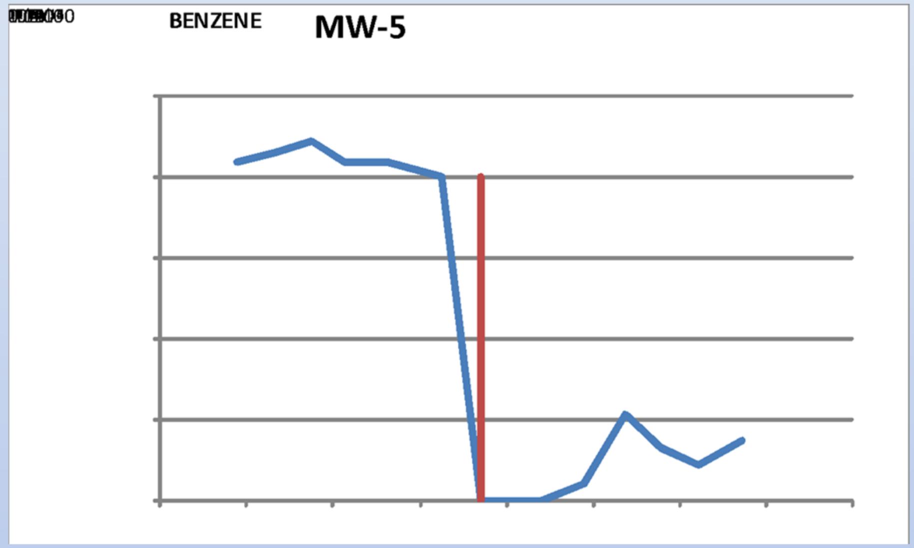
Instant response

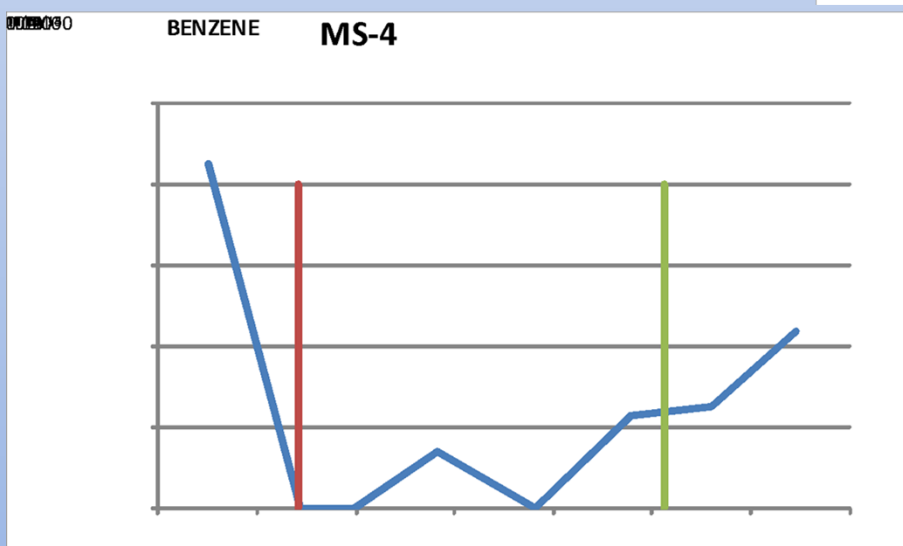
Slower response



Typical well responses after CBI:

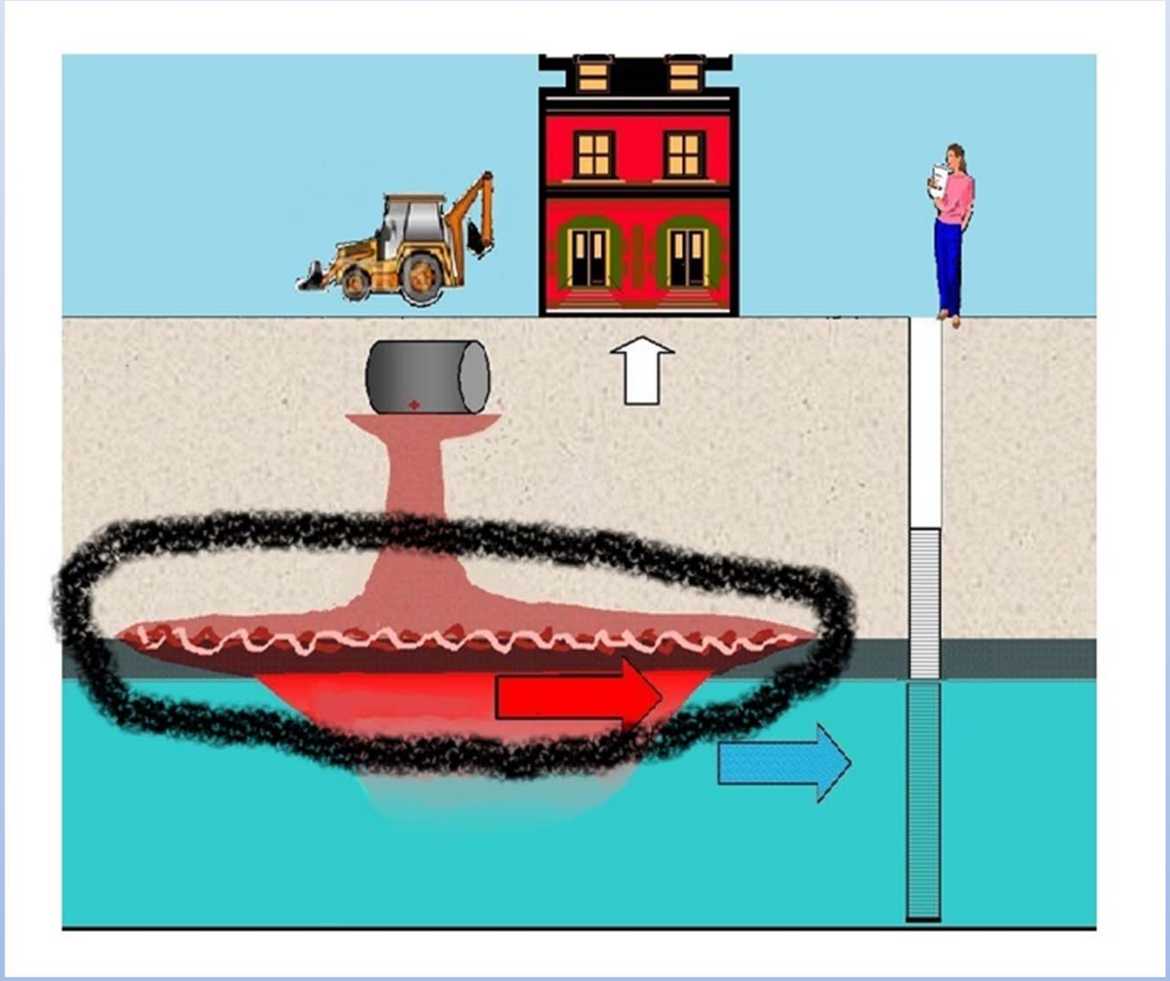
Rebound





Rebound after pilot plus second injection

4. Methods of Application



Installation into the smear zone
areas slightly above, within, and below the water table

Methods of Application

- Gravity Feed: advection and dispersion
  (not recommended—too slow and limited area)

- Pressure Injection below fracture pressure:
  The amendment must be on a molecular scale smaller than soil pore throat size.

- Pressure Injection above fracture pressure:
  Makes new openings and follow regions of less resistance
  - Build-up pressure vs Immediate pressure

- Direct application to excavation and trenches
  (best way to guarantee distribution)

Methods of Injection

❑ High pressure jetting (soft materials)

- Similar to grouting process for soil stabilization
- Extremely high pressure (5000 psi) to homogenize amendment and soils
- Applied where hydraulic fracturing is less practical or ineffective (e.g., sandy material)

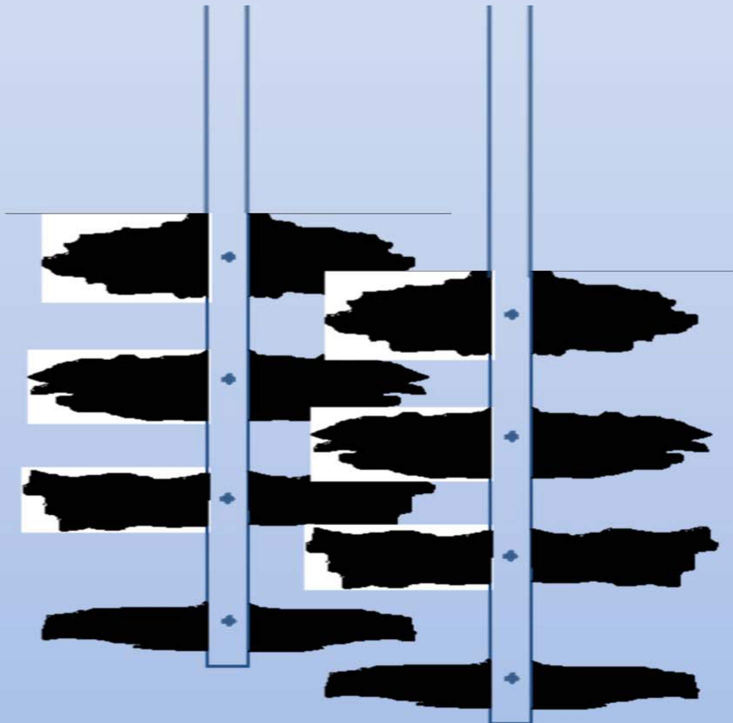
❑ Hydraulic fracturing (hard materials)

- Requires borehole installation
- Fracture initiation by notch or water jetting
- Sand or guar gum usually mixed with amendment as slurry to keep fracture open

High pressure direct push injection (DPI)

- Has become the most widely used technique for carbon injection
- Direct push rig (e.g., GeoProbe)
- Various designs for injection tip
- Tight spacing (5-7 ft hex grid), 1-3 ft vertical interval
- Initiation pressure is generally greater than 100 psi, typically 300–600 psi in low K zones (fractures), then drops as fracture propagates at 25-100 psi tight grained,
- Flow rates <1 gpm to 75 gpm (35 to 75 typical)

Alternate Injection Intervals Vertically using Hexagonal Spacing Horizontally

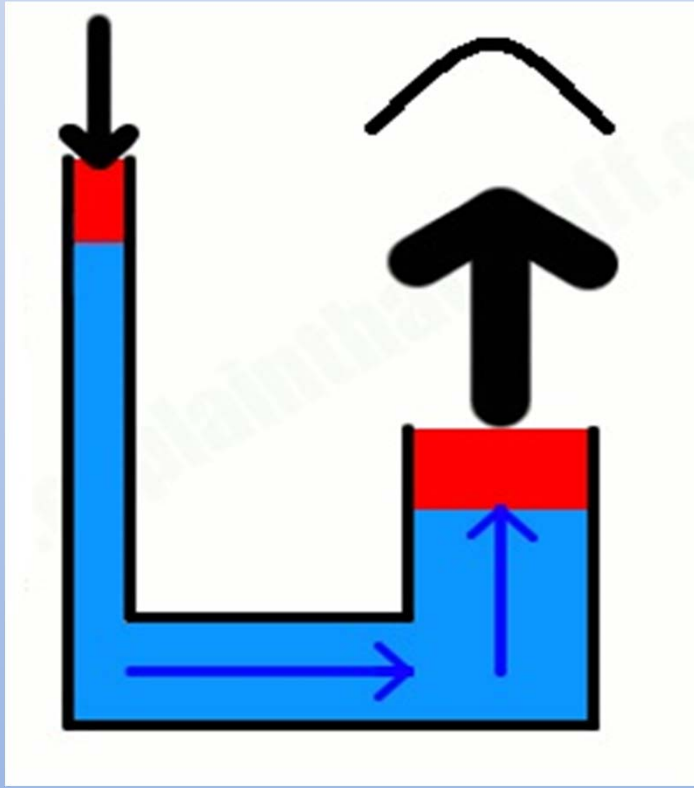


SIDE VIEW

Activated Carbon as “Particle”

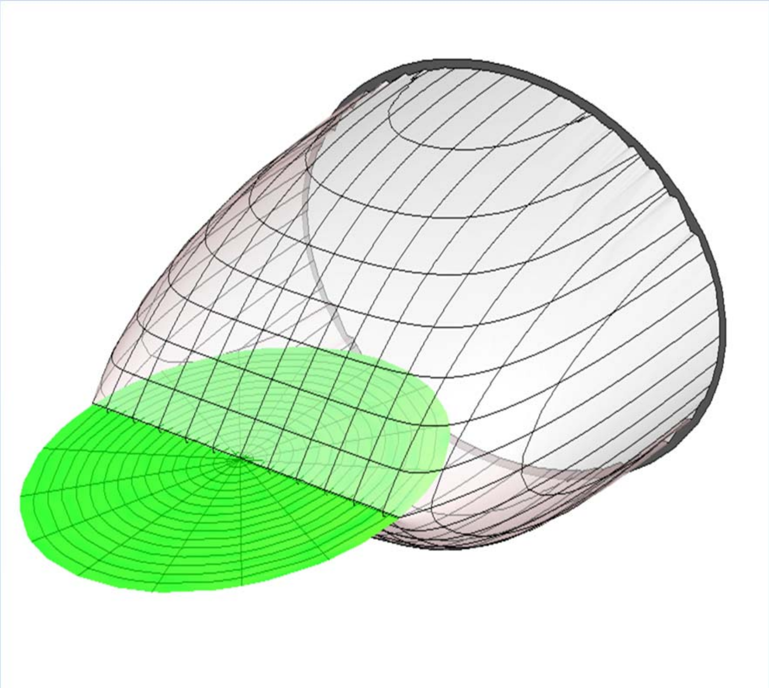
Increased mass in subsurface:

Results in uplift



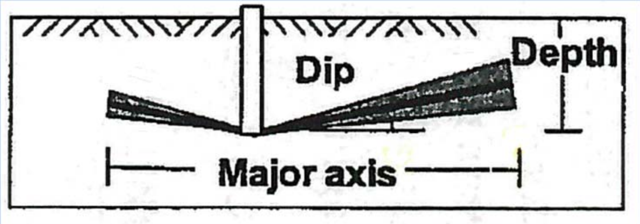
Altering of micro and meso flow dynamics: Local Tortuosity.

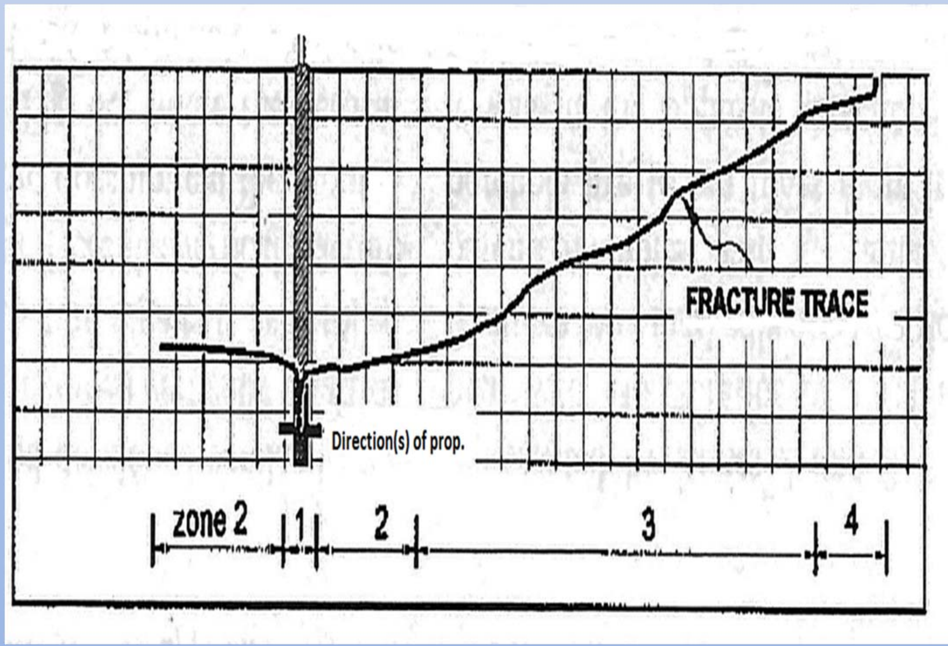
Global flow dynamics remain the same



A bit about fracture emplacement

- Emplacement every 5 to 7.5 ft
  ~10-25 cm (Christiansen, 2010)
- Ideal ratio is 3 ft horizontal for every 1 ft vertical
- Practical ratio is 1/1 up to 2 m
- Pressures ≈100 to 700 psig
- Daylighting occurs
  – Degree is site specific
    - Could be 20% on sites with previous drilling and infrastructure paths
    - ≈ 3 to 5% daylight around the rod
  – Soil conditions
    - Saturated soils





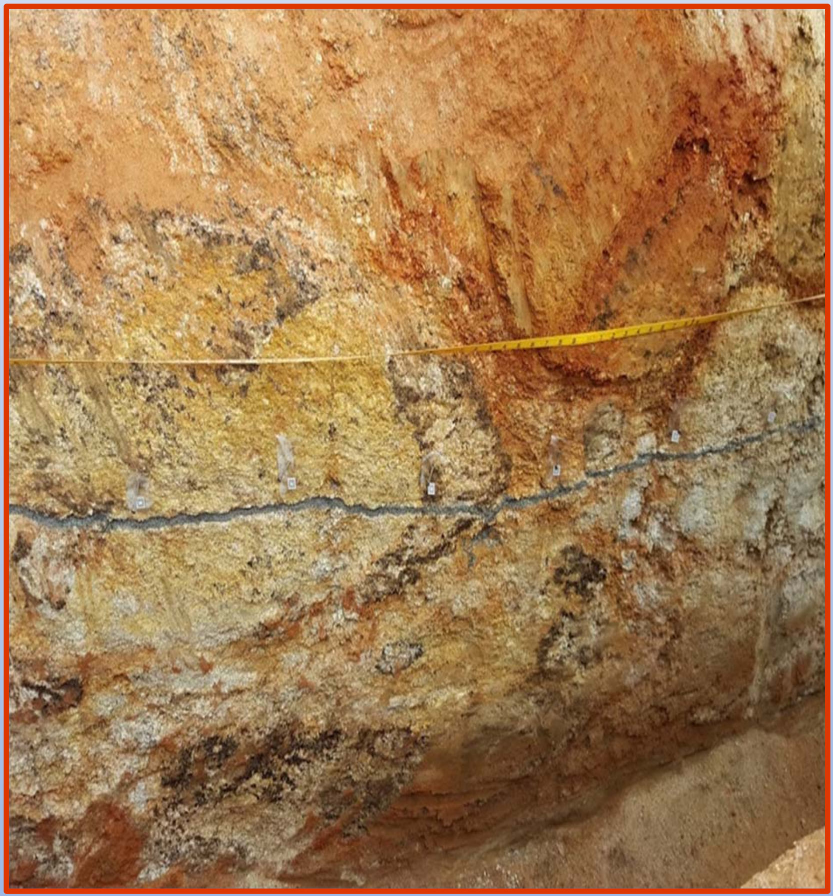
Top right picture: Murdoch & Slack, 2002.
Bottom right: Murdoch, 1995.

Distribution is based on physics and has a general pattern that is predictable

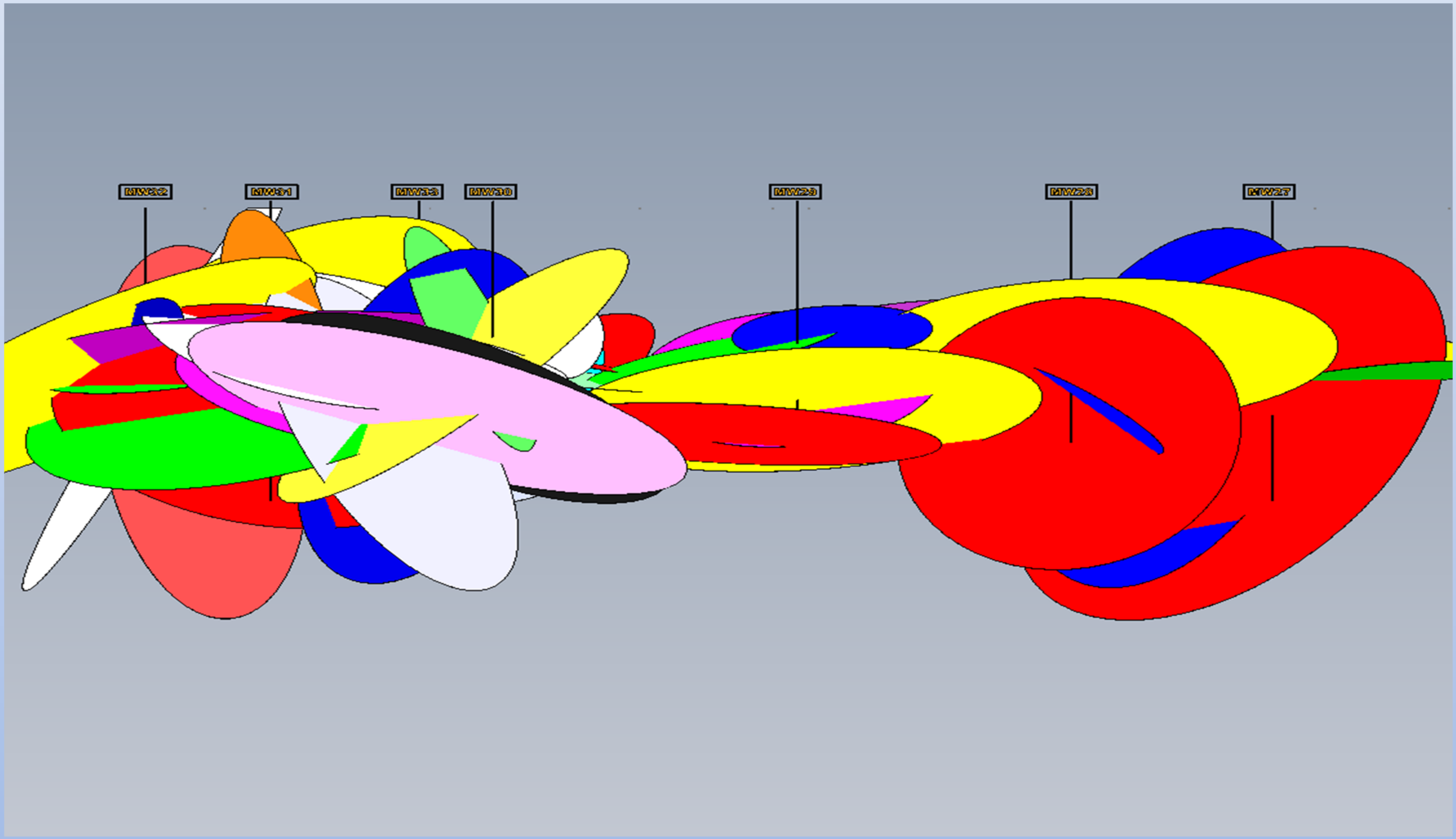
- Jell-O animation

https://youtu.be/2UHTj9mn7h4

https://youtu.be/Jsf0Wa0U1tc



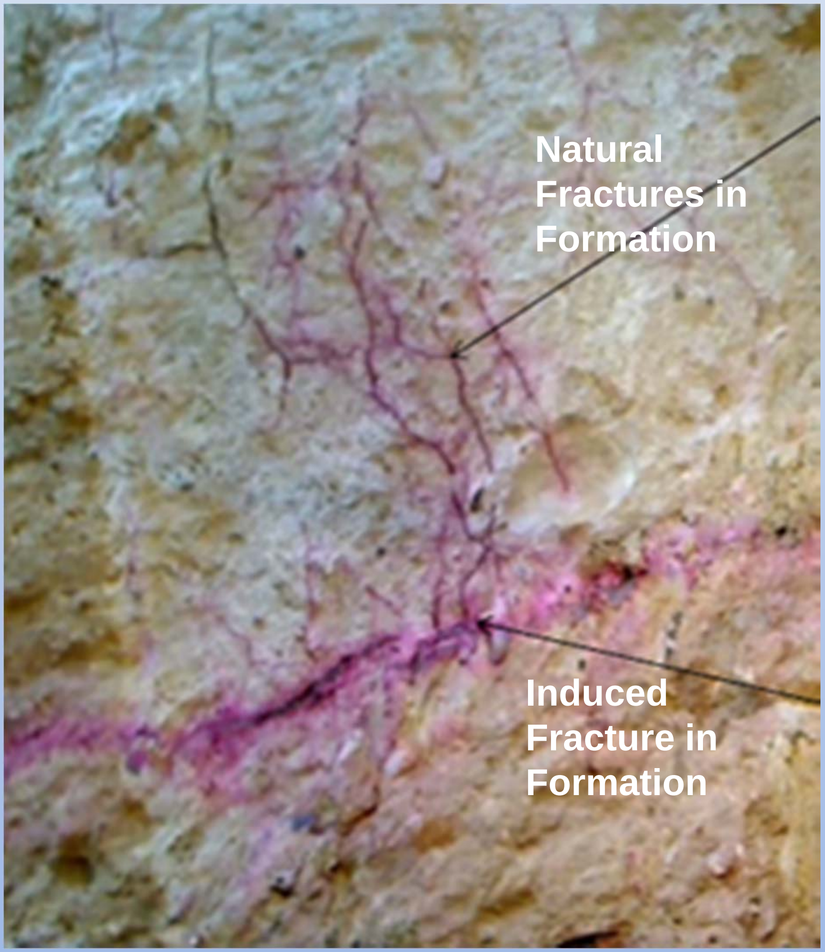
Idealized Fracture



Frac Rite, Geo Tactical, etc.

Look Closer: Random Characteristics

Different Sites and Techniques



Seemingly small seams

can fill larger voids

Patterns Seen in Various Soils

Thin veins

Spots

Homogenization

5. How Much to Inject?

Quantity/volume per interval based on amount of carbon necessary to:

1. adsorb the mass of contamination
2. build a treatment field (distribution)

Target injection intervals using HRSC!

(Injection **point** is horizontal while an injection **interval** is vertical)

Total Mass = Total Hydrocarbon x Volume of Contaminated Media

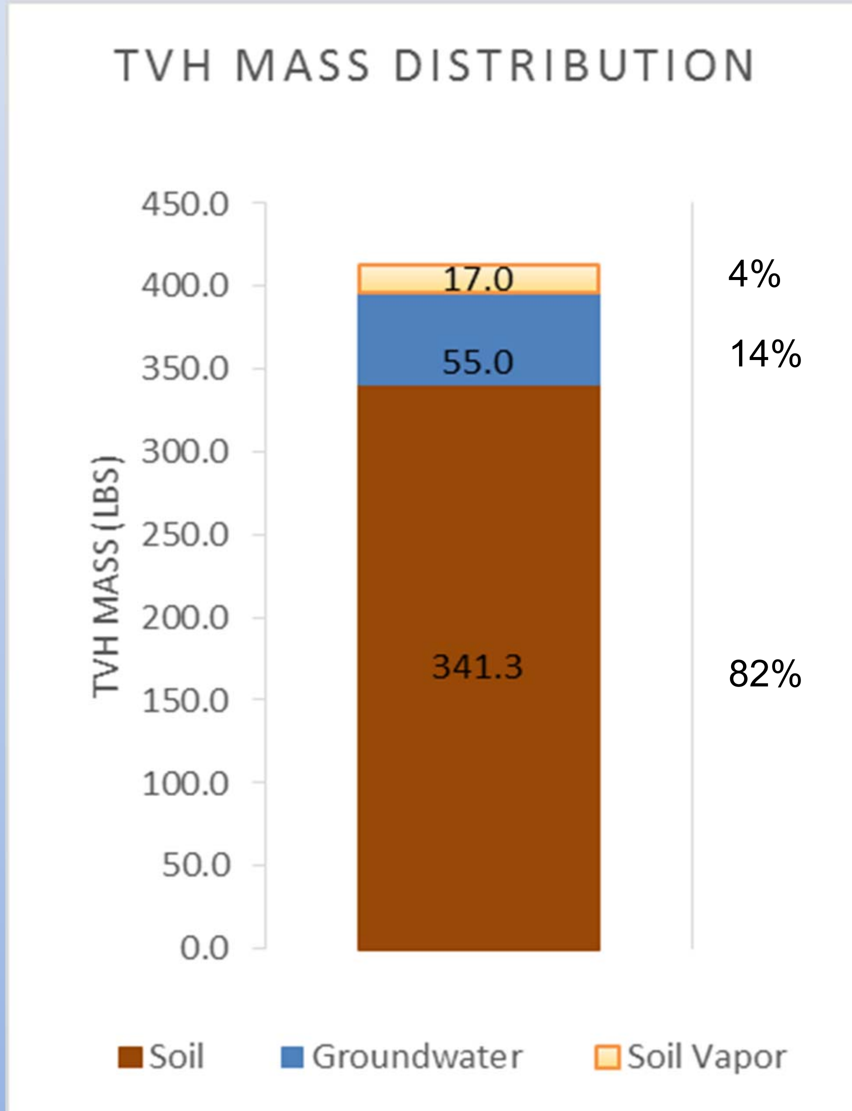
Accuracy Depends on:

- ❖ Concentration Data Collected x
- ❖ Correction Factor (TPH vs BTEX) x
- ❖ Volume of Contaminated Mass (Soil, Water, Vapor) x
- ❖ Value for Error (your safety factor)

Importance of TPH Mass in Soil

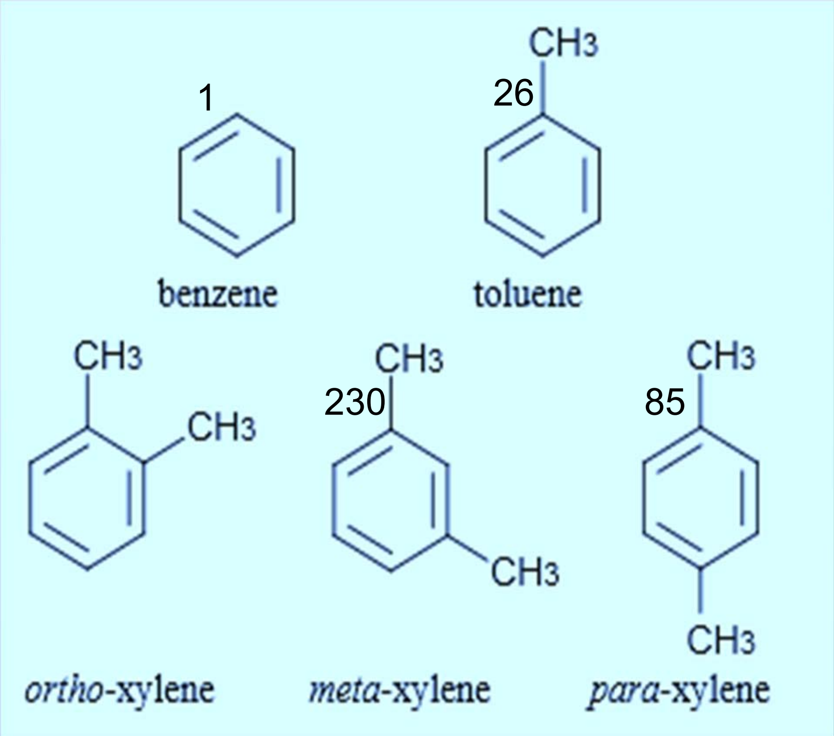
Soil holds the majority of the contaminant mass.

An adequate number of soil samples is critical (even below water)



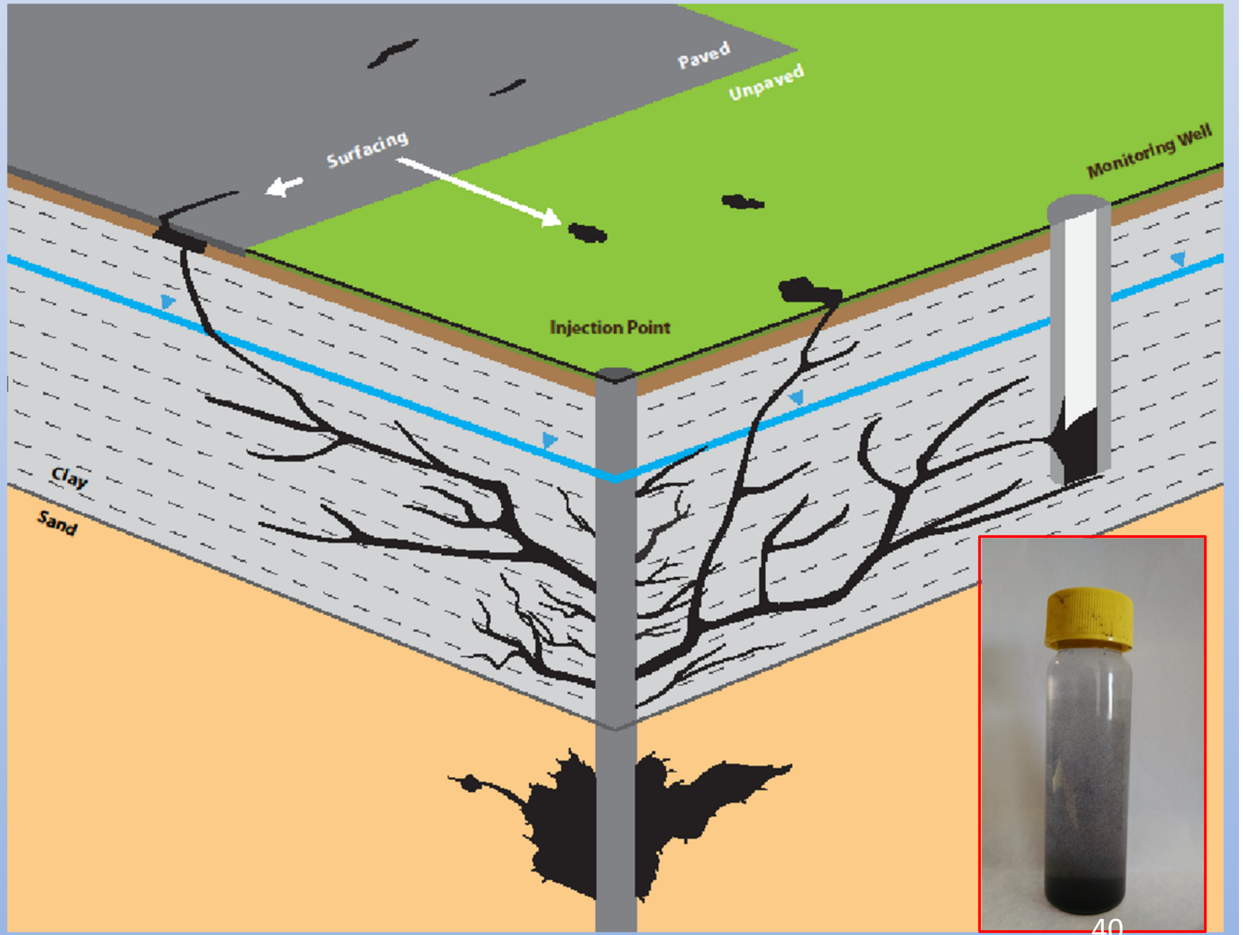
Benzene is not a major component of gasoline, and it is not adsorbed preferentially.

- Mass fraction in weathered gasoline: benzene 0.2%; m-xylene is 3.8% (Ground Water Management Review, Spring, 1990, p.167).
- The adsorption isotherm (K) m-xylene is 230 mg/g versus 1 mg/g for benzene
- So, <u>benzene is displaced by most other constituents</u>.

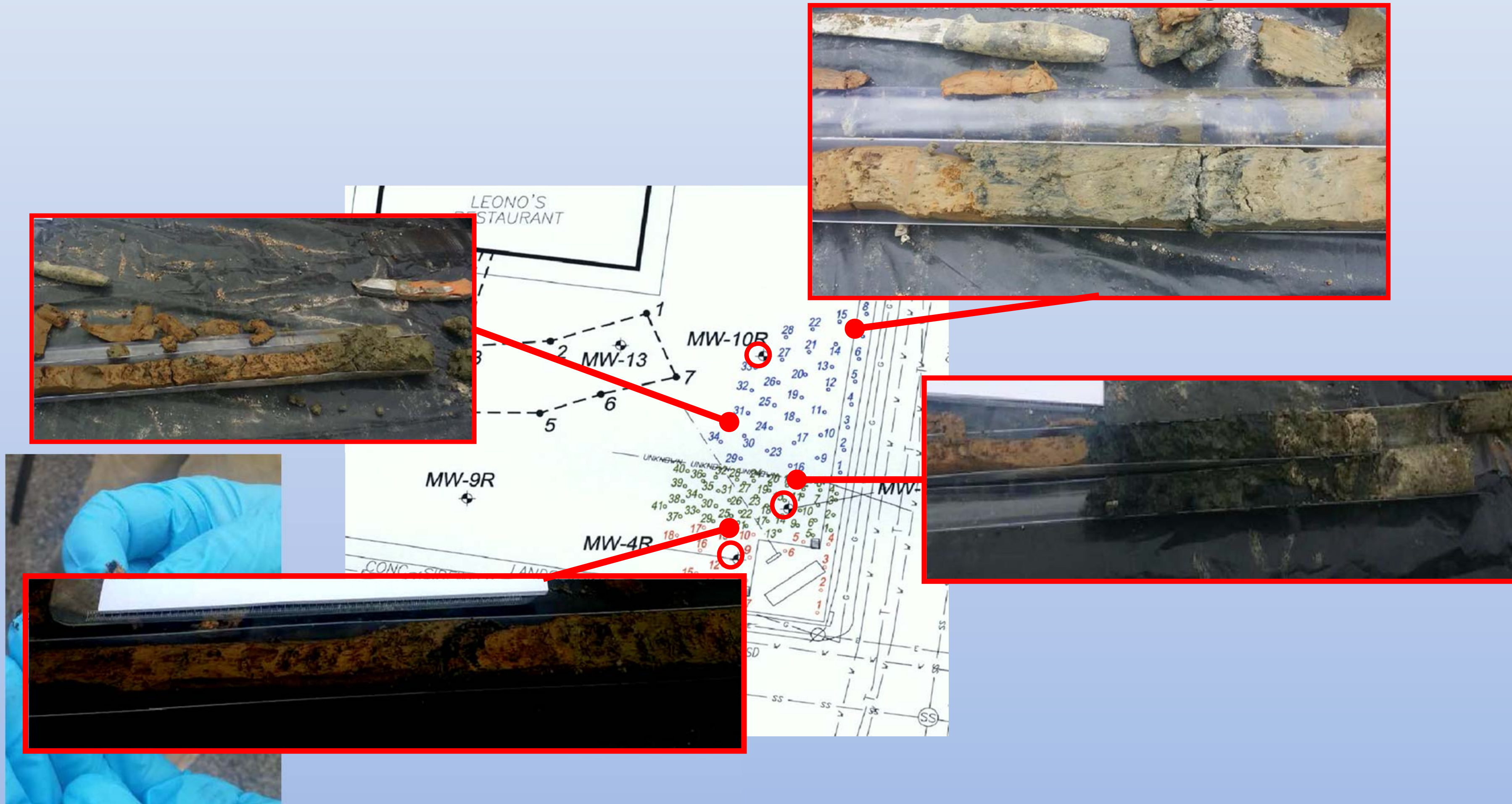


6a. Injection (Distribution/Absorption) Issues

- How to get it distributed?
  - ✓Daylighting to surface
  - ✓Entering utilities or backfill
- Entering monitoring wells
  - ✓Rehabbing wells
  - ✓Well replacement
- Does CBI displace contaminants?

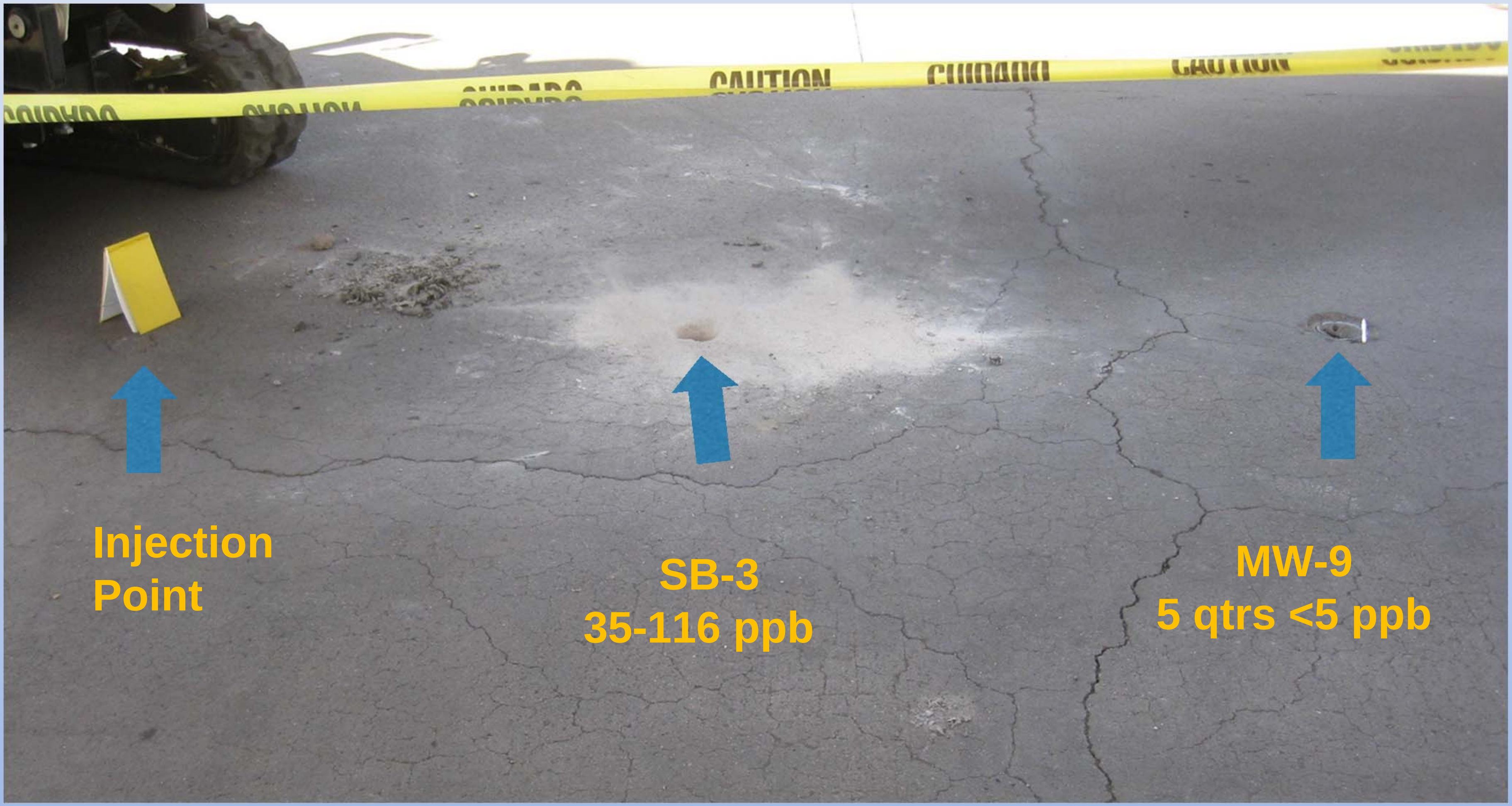


Case Study (KY):
Distribution in Low Permeability Unit

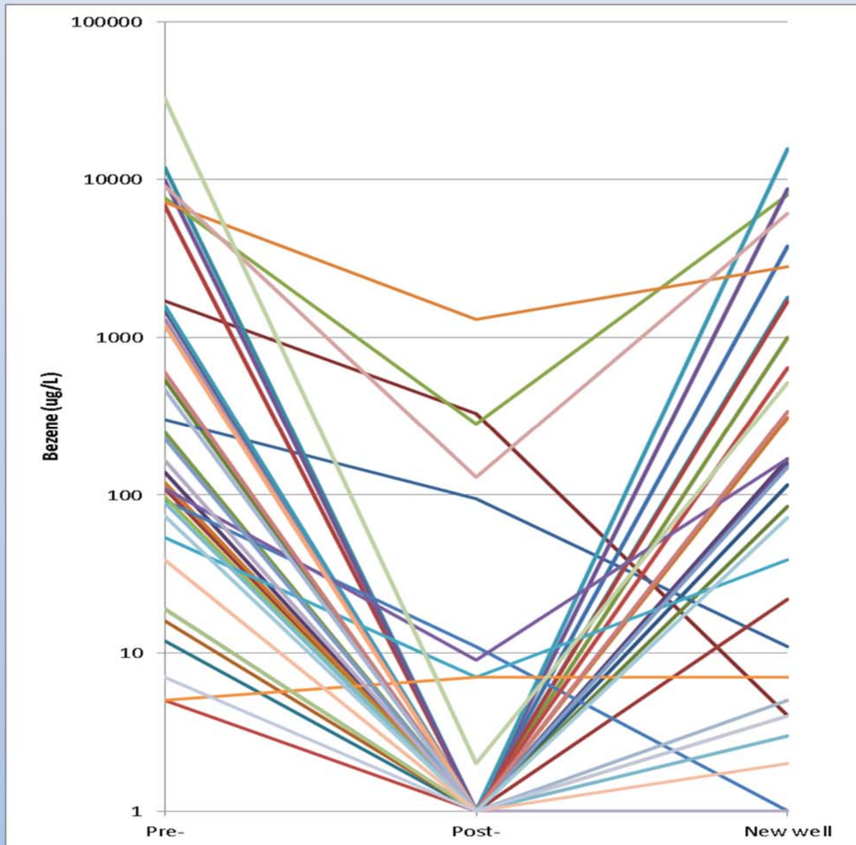


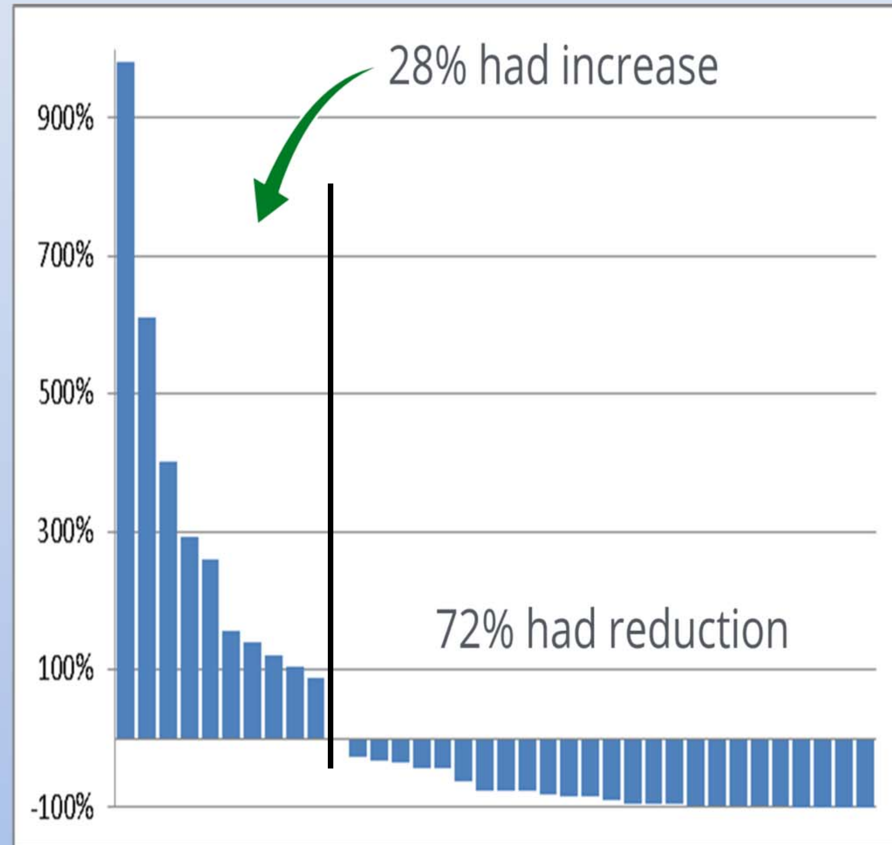
- Carbon detected in groundwater monitoring wells (open circles) and in soil and groundwater from temporary wells (closed circles) between injection points.

Groundwater samples



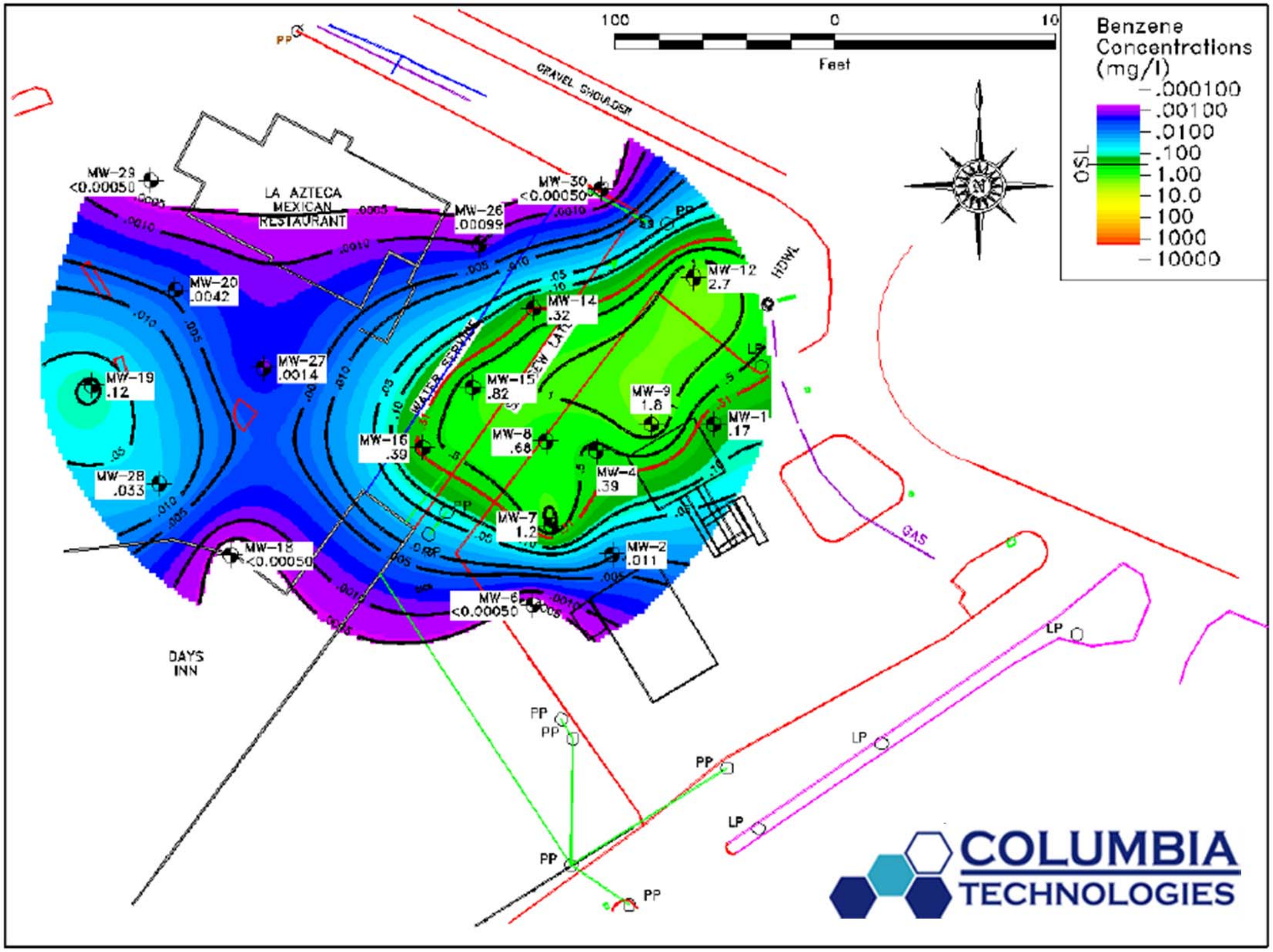
… aquifer treatment incomplete?



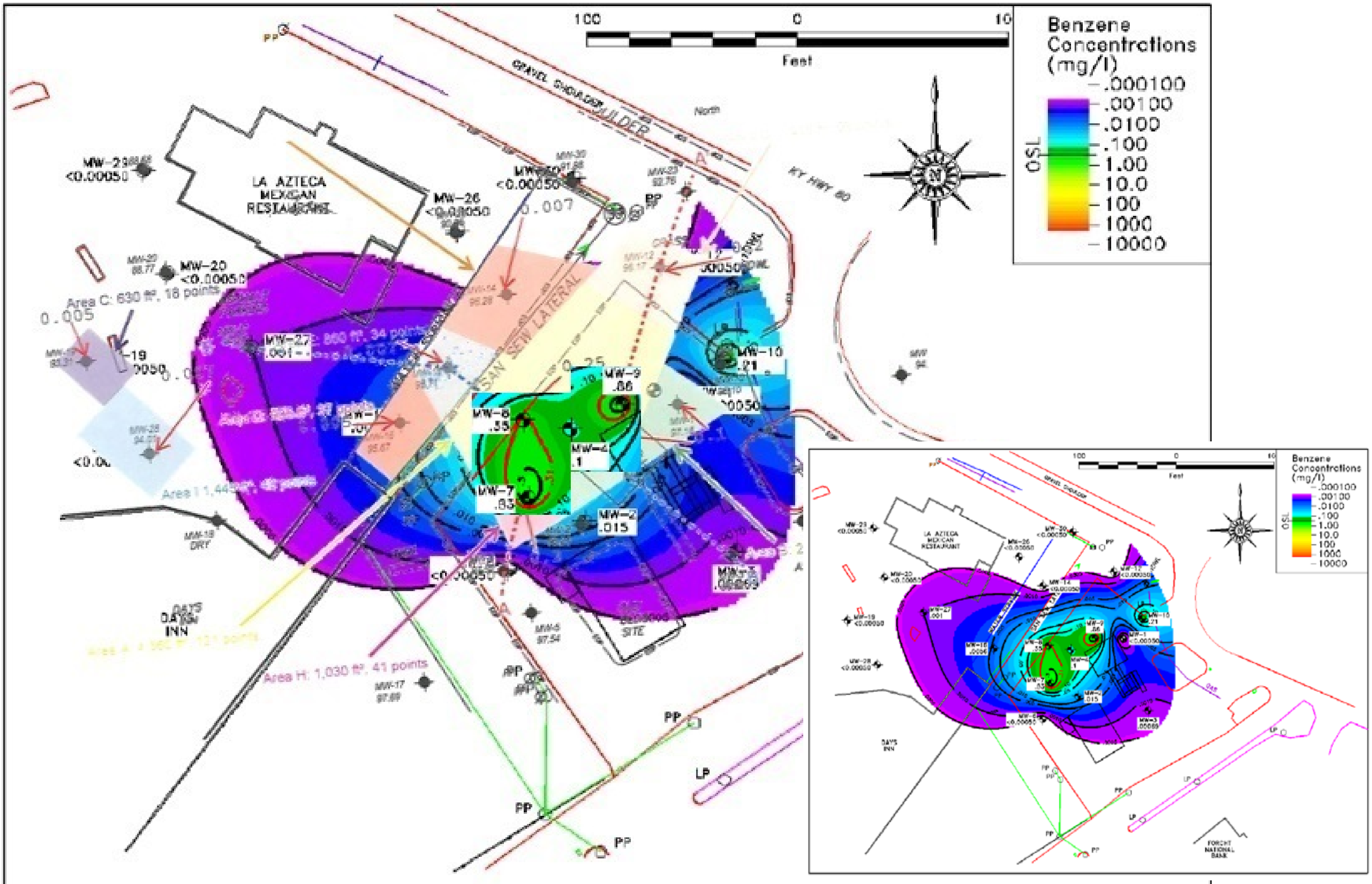


(36 well pairs)

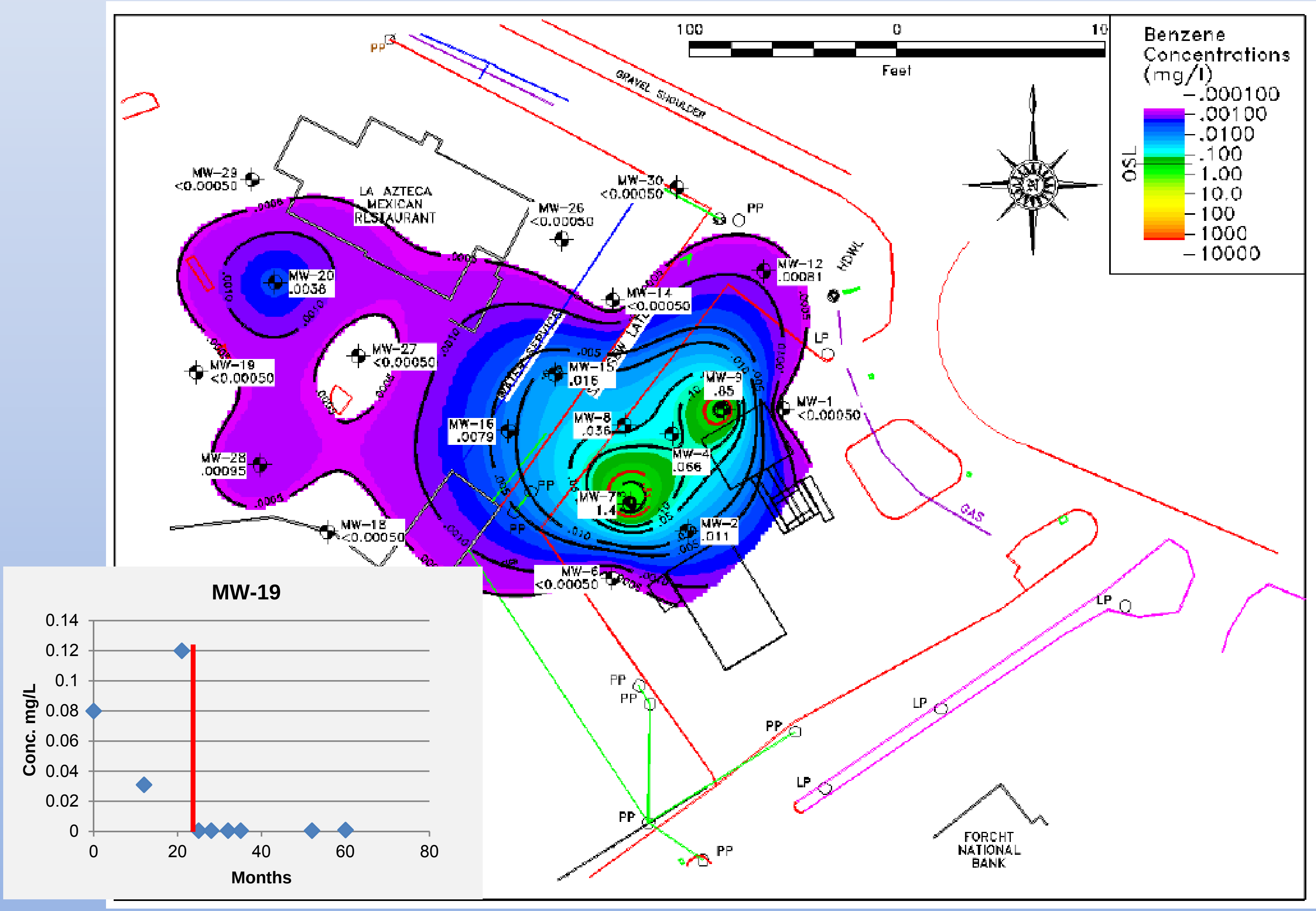
Benzene Conc. Pre-injection Monitoring Well Data 05/13/2013



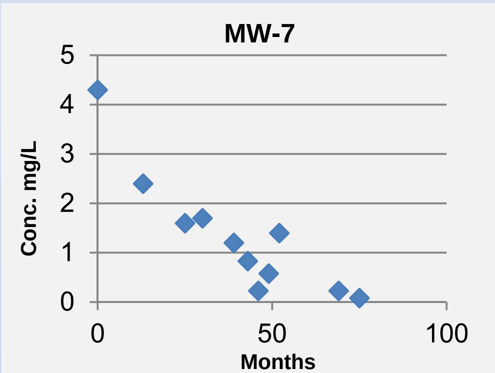
Benzene Conc. Post-injection Monitoring Well Data 09/20/2013

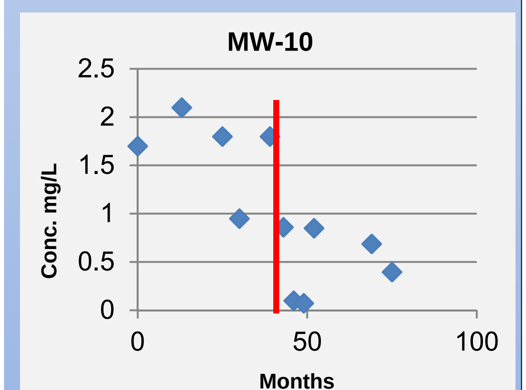


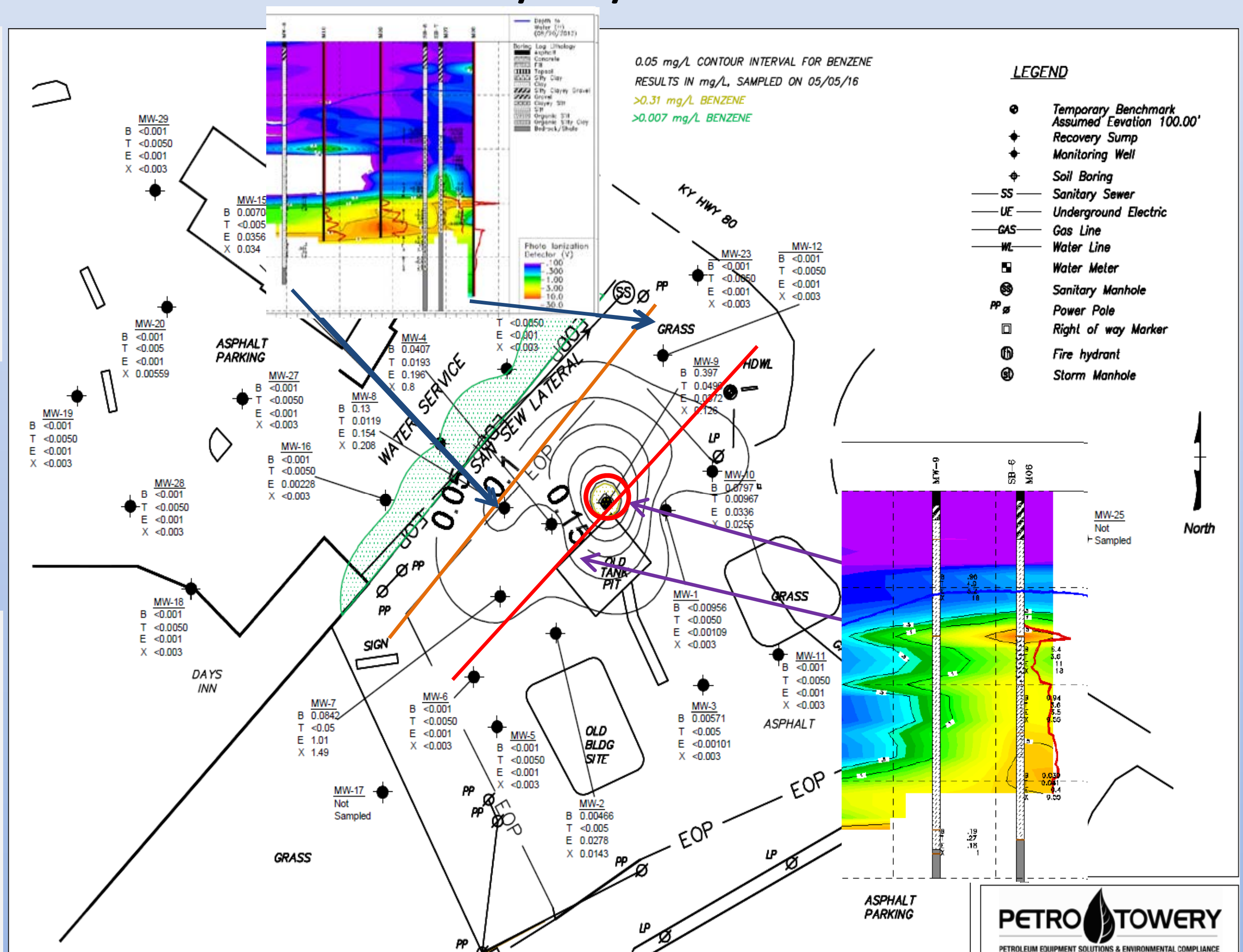
Benzene Conc. Post-injection Monitoring Well Data 06/19/2014



Benzene Conc. Post-injection
Monitoring Well Data 04/05/2016
MIP Data from 03/04/2015







6. Degradation (Regeneration) Issues

Expectations associated with microbial biodegradation:

- AC provides a substrate for indigenous microbes or supplies
- A treatment field constitutes a new “ecosystem”, additional “territory”
- New ecosystems like new gardens have to be nurtured (assertion)
- AC can function in-situ for decades

1. How long do adsorption effects last?
2. Does in-situ regeneration by biodegradation occur, and for how long?

Why does "rebound" occur?

1. Poor site characterization to target contaminants.
2. Poor AC distribution (injection).
3. AC overwhelmed - insufficient AC mass applied.
4. Preferential desorption occurring (chemistry).
5. Degradation processes don't keep up with desorption from impacted soil (rate limiting).
6. Degradation processes slow or stop (longevity) due to
   - ❑ insufficient inorganic nutrients
   - ❑ inappropriate environment (e.g. temperature)
   - ❑ lack of degraders

In-Situ Degradation Requires Further Investigation

- Engineered systems and lab studies demonstrate the science, *but they do not assess field conditions*.
  - Complex hydrogeological conditions
  - Presence of indigenous microbial community
  - Dynamic adsorption/desorption
- Few field parameters can be used to directly prove biodegradation.
  - Concentrations of electron acceptors (e.g., nitrate, sulfate)
  - Concentrations of CO_2 and other respiration products
- Characterization of microbial community (species?) associated with activated carbon might be a viable way to demonstrate biological activity.

7. Recommendations

1. Complete a full and detailed **site assessment** to precisely locate the horizontal extent and vertical zones of contamination. Do continuous soil sampling, MIP, etc.
2. Do contaminant **mass calculations** for dissolved and adsorbed contamination to ensure an adequate amount of carbon is injected where needed. (CBI is not useful in the vadose zone.)
3. Understand the basis of design and use an **experienced design team and installation contractor**.
4. Pilot testing is recommended. Surfacing and well impacts are not indicative of radius of influence.

Recommendations

5. Inject over **short (1-2 ft) intervals** for the best control of carbon distribution. Treat the entire **vertical interval of contamination**. (Don’t assume uniform treatment)
6. Improve monitoring protocol:
   - Stop injections upon surfacing / well impact.
   - Characterize other biogeochemical parameters to understand field conditions (environment).
7. Well **rehabilitation doesn’t work**. Confirmation soil borings and wells likely needed.
8. Add **more nutrients** (frequently) to boost biodegradation probability.

Conclusions

- CBI is a promising in-situ remedy for subsurface cleanup at UST sites.
- Follow detailed assessment practices, particularly high resolution CSM.
- Injection experience is critical.
- Despite strong scientific principles, more research needed on the long-term effectiveness of contaminant adsorption/degradation in field applications.

Questions/Discussion

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Thank You