High Resolution Injection of Activated Carbon, Nutrients, and Bacteria to Super-Stimulate Aerobic and Anaerobic Remediation of Petroleum Release Sites for Faster Site Closure

John Fontana, PG
President & CEO
Vista GeoScience, Golden, Colorado, USA

22nd International Petroleum Environmental Conference
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Grand Hyatt in Downtown Denver

Outline

- **Data Needed to Design a Treatment**
  - **Remedial Design Characterization (RDC) Tools**
  - **3-D Qualitative and Quantitative Data**
- **Activated Carbon+ (Specifically RPI BOS200®)**
- **Specialized Tools for Highly Targeted Injections**
  - **Why the “Old Methods” Don’t Work**
  - **The Right Tools and Methods**
- **Recent Examples**
- **Summary & Conclusion**

Why In-Situ Injections

- **Limited or No Disposal Issues**
- **In Place Destruction of Contaminants**
- **Less Invasive - Works Around Infrastructure**
- **Many Work with Natural Environment**
- **Direct Push Injection Advancements**
- **Improved Understanding of Hydraulic-Fracturing**
- **Improved Monitoring Methods,**
- **So….. Seen as Faster, Cheaper *and it's……***

Greener & Sustainable Technology!

The Need?

Site Closure from One Final Treatment Design

The How:

1. **Remedial Design Characterization (RDC): Collect both Qualitative and Quantitative High Resolution Data.**
2. **Pilot Testing**
3. **Apply the In-Situ Treatment: Use Precise Injection Designs, Adequate Pumps and Proper Tools.**

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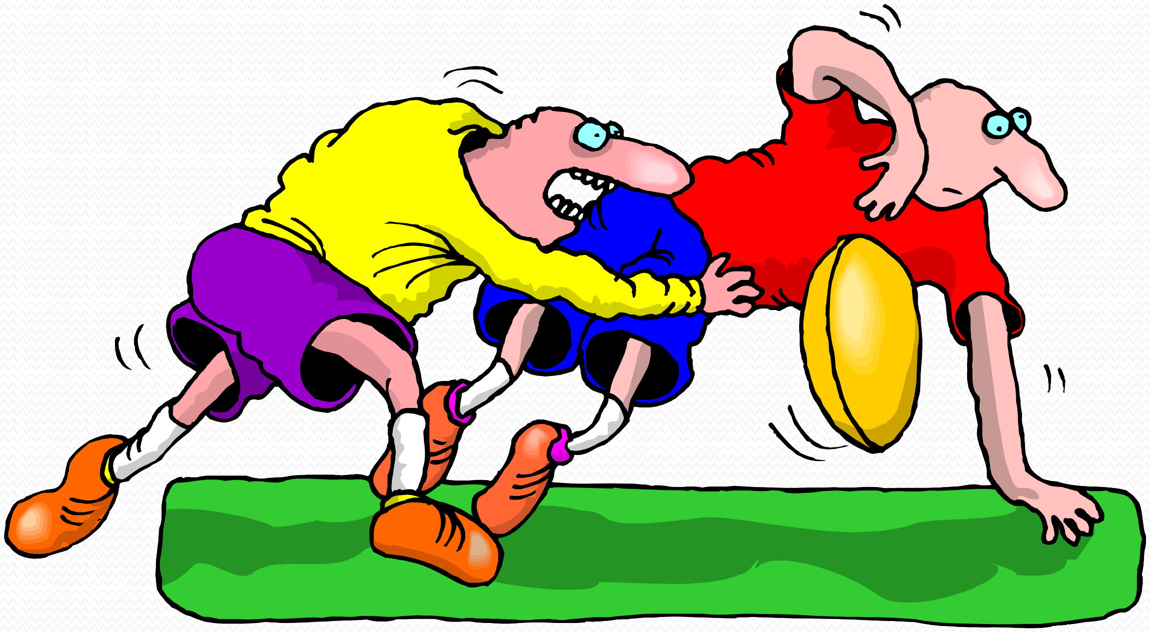
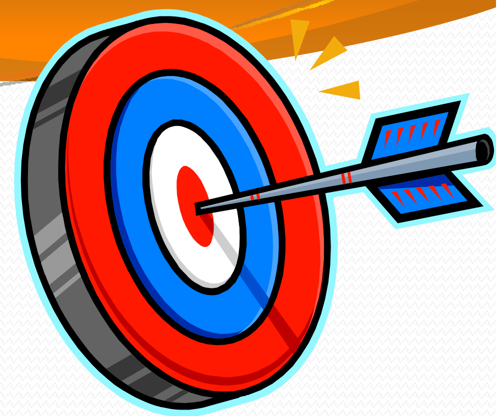
In-Situ Remediation:
It's a Contact Sport!

- **HOME TEAM: Contaminated Soil & Ground Water**
- **VISITING TEAM: Treatment Reagents**



The Goals of a RDC



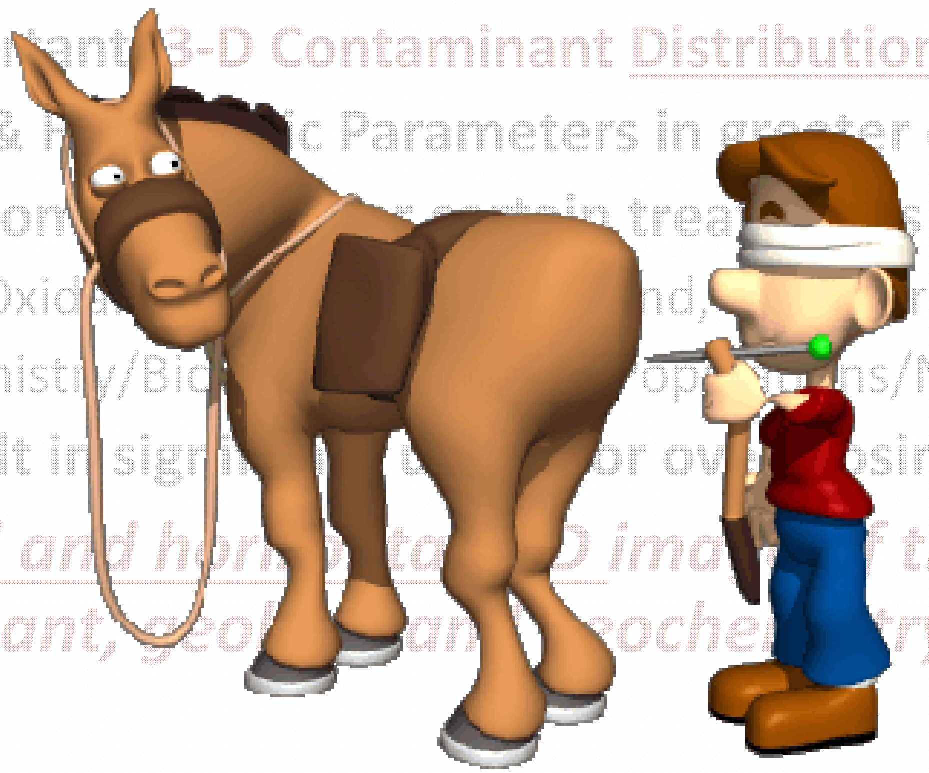
Determine:

- **Where the Contamination is Located**
  - **Vertical and Horizontal Distribution**
- **How Much Mass is There to Treat (Dosing)**
- **Physical, Chemical & Biological Parameters as Needed for Specific Treatments.**
- **If Soil/Rock Types, Heterogeneity and Back Diffusion Affect the Choice of Methods**

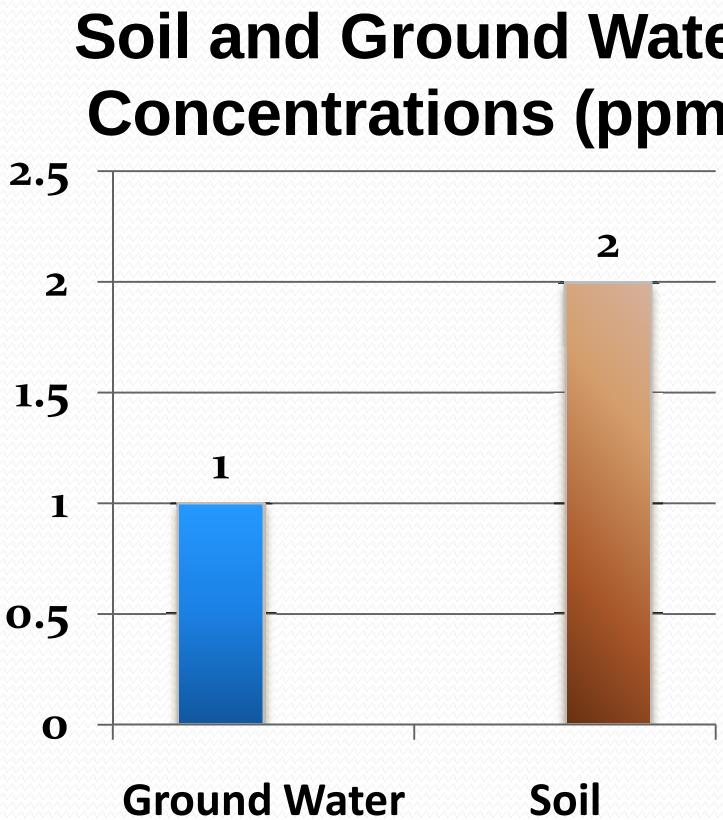
Remedial Design Characterization - Critical for Success

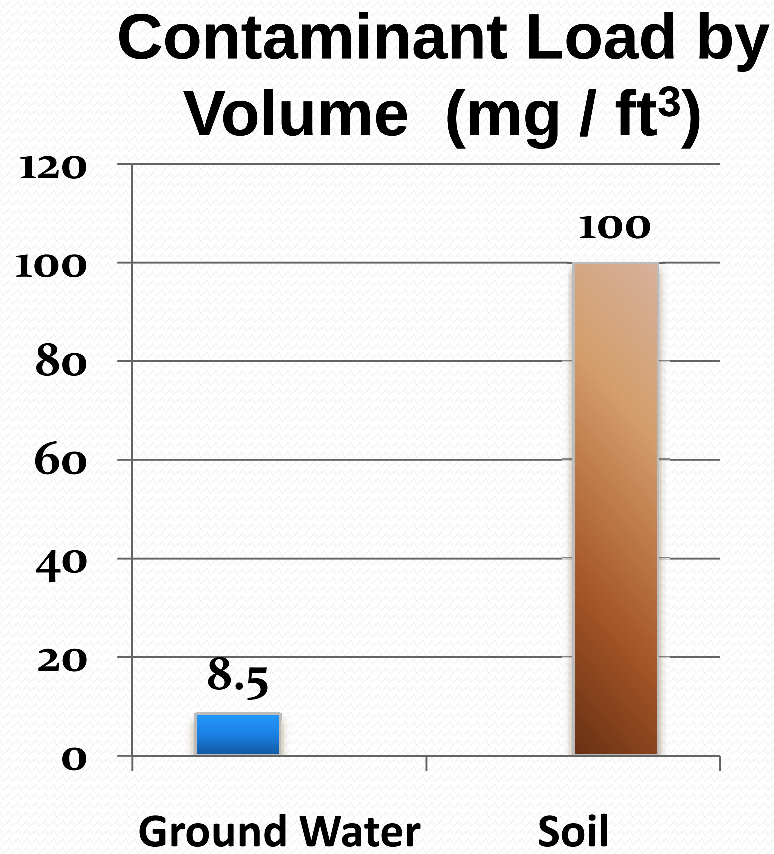
Don’t Be Blindfolded and Miss the Target

- Yes, in 2-D, but we need more data for the Remedial Design!
- Most Important: 3-D Contaminant Distribution *and* Mass
- Lithologic & H… c Parameters in greater detail
- Chemical Con… certain trea… s is unknown
  - Natural Oxid… nd, … rs & Acceptors
  - Geochemistry/Bio… op… ns/Nutrients
- Errors result in sign… or ov… sing – or both!
- *A vertical and hor… ta… D ima… f the site contaminant, geol… an… geoche… try is required!*



ISSUES: Adsorbed Phase vs. Dissolved Phase Contaminant Loading





If you design to only treat the dissolved phase contaminant, you get REBOUND

Back Diffusion from Clays = REBOUND

(Consider Mass Flux Discharge in RDC)

Courtesy Tom Sale, PhD, Colorado State University (Go RAMS!)

High Resolution Site Characterization (HRSC)

Tools for Remedial Design Characterization

- ✓ **Direct Sensing Probing Tools**
  - ✓ **MIP, HPT, LIF, EC, Cone Penetrometers, etc.**
- ✓ **High Resolution Sampling Methods**
  - ✓ **Discrete Soil Core and Discrete Ground Water Sampling**
- ✓ **Determine the mass and distribution**
- ✓ **Other Investigation Tools/Methods**

High Resolution Direct Sensing Investigation Tools

Membrane Interface Probe (MIP) at the Denver Federal Center

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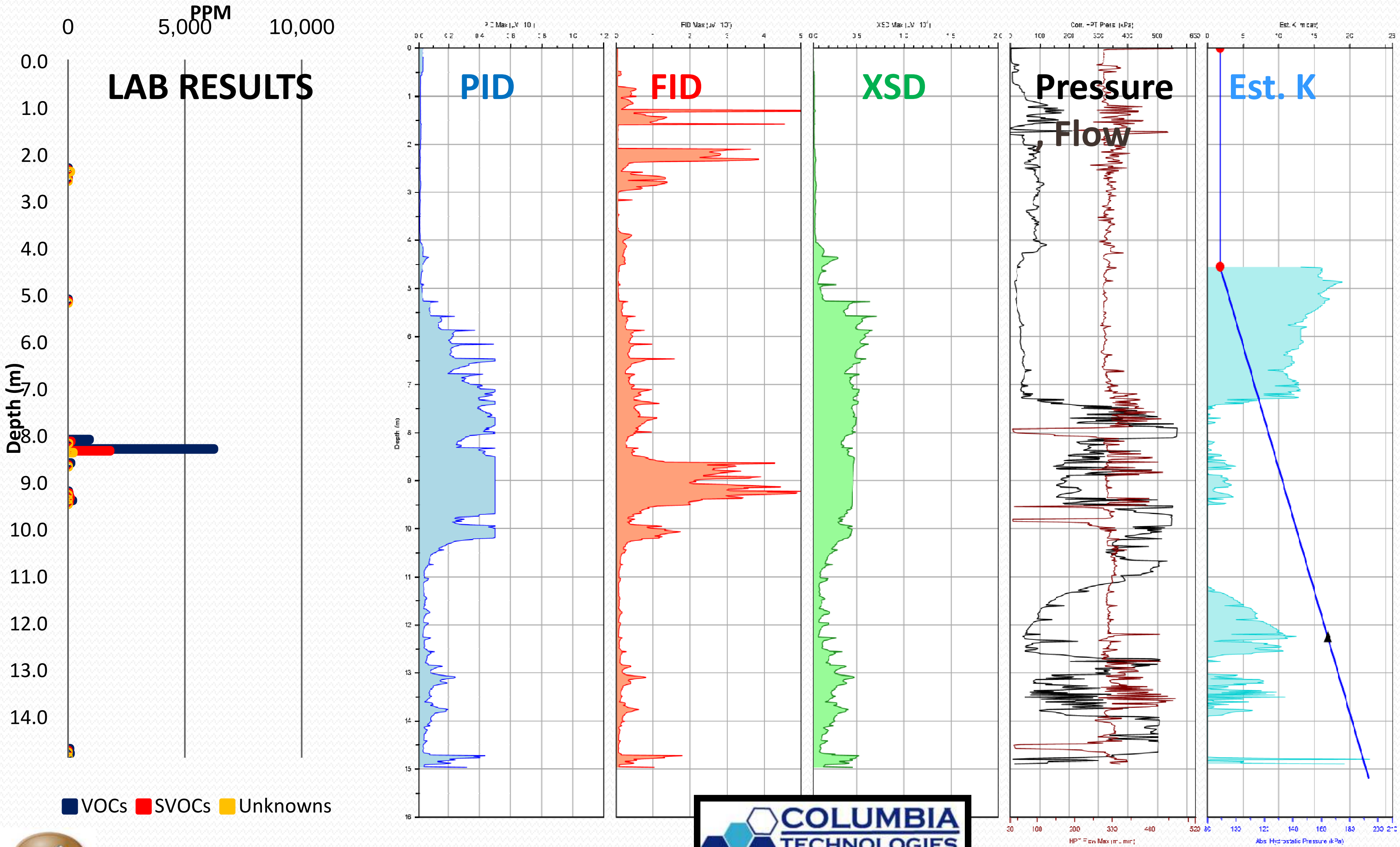
High Resolution = Millions of Data Points

MiHpt Log - Tracking SVOC DNAPL



COLUMBIA TECHNOLOGIES

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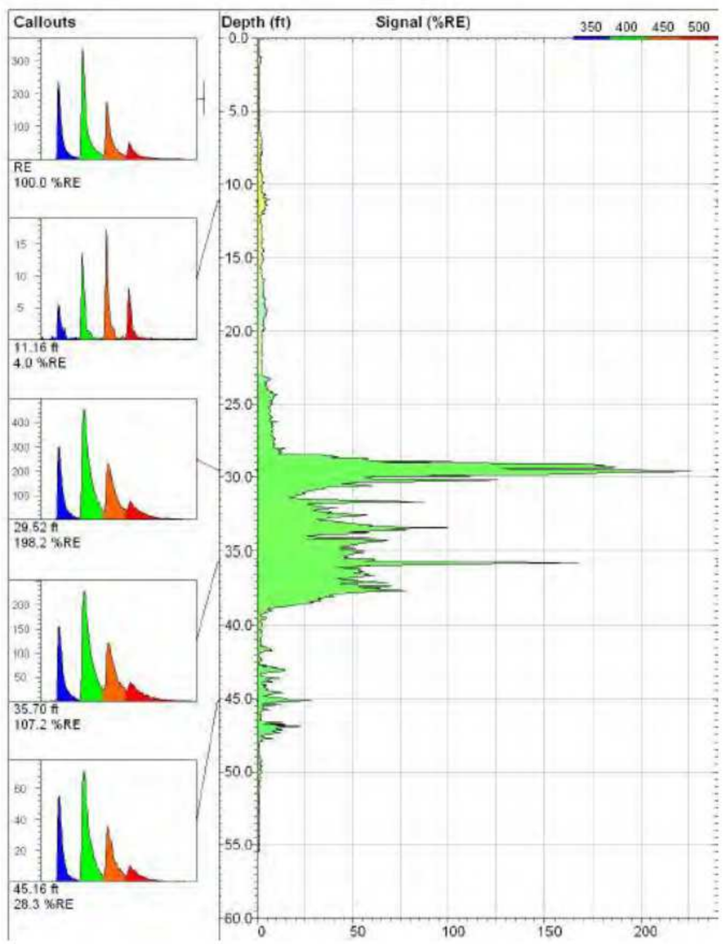
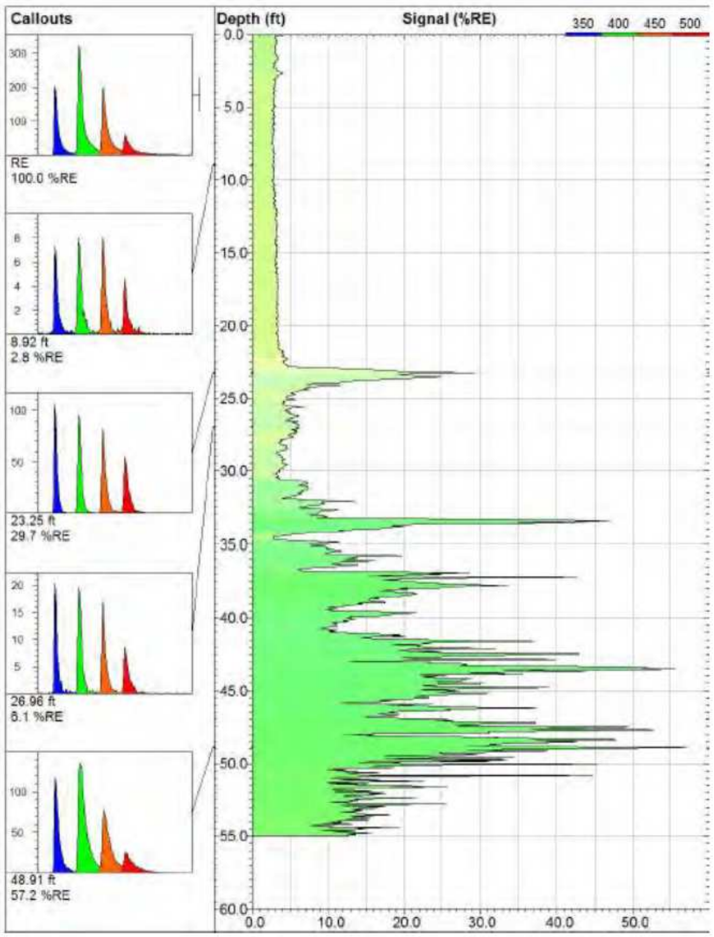
Laser Induced Fluorescence (LIF) Logs

(Ultra Violet Optical Screening Tool – UVOST)

LIF Logs





High Resolution Sampling

Low Tech: Required for *Quantitative* Analysis of Mass Present

- **Dosing Calculations Required Contaminant Mass.**
- **Continuous Cores Samples, Composite Samples**
- **Discrete Ground Water Samples**
- **Quantitative Lab Analysis of VOC, TPH, Nutrients**
  - **(Can be screening level data vs. definitive data.)**

Representative Sampling from Continuous Soil Cores

(Remember: A saturated soil sample includes the pore water, and therefore the combined adsorbed and dissolved phase)

Sub-Sampling Continuous Cores for VOCs Using Plugs

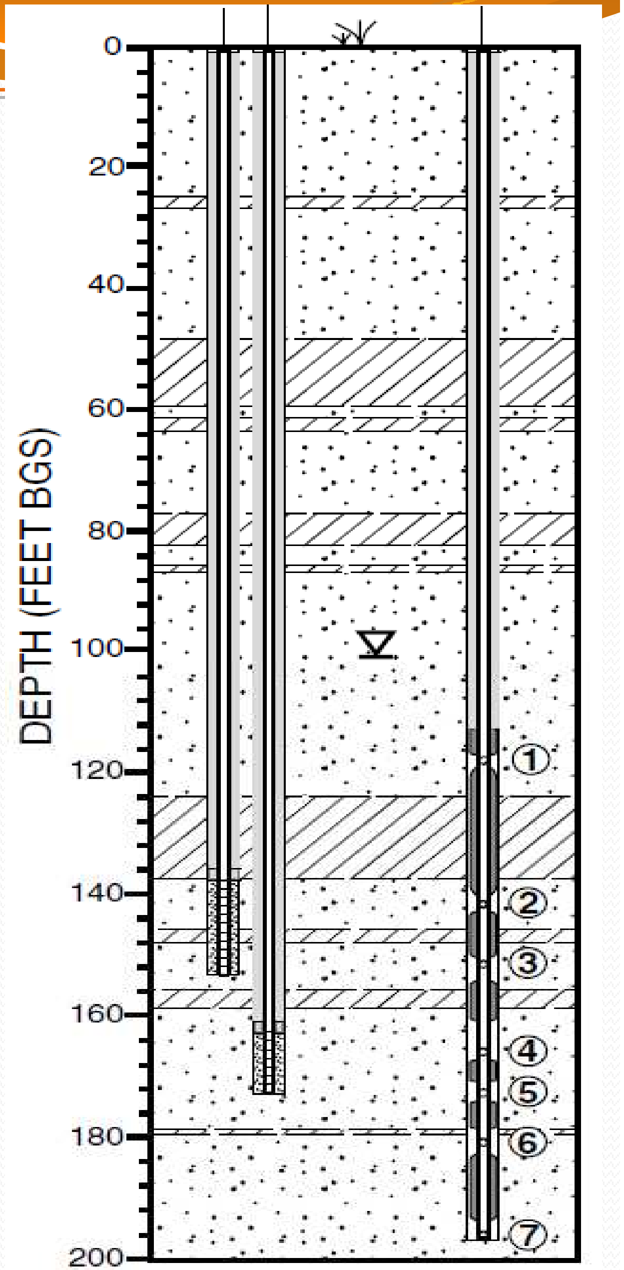
Cutting a Composite "Wedge" from the Continuous Core

ITRC (Interstate Technology & Regulatory Council). 2012. *Incremental Sampling Methodology. ISM-1. www.itrcweb.org.*

Tools for Discrete Ground Water Samples

- Discrete GW Sampling Tools
- Multiple Wells with Discrete Screens
- Single Well with Multi-Level Ports
- ….BUT REMEMBER: 80-90% of the mass resides in the saturated soils.

Geoprobe® Screen-Point Sampler



Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring, Second Edition, Ed. David M. Nielsen –
CH 11, Multi-Level Ground Water Monitoring, Murray Einarson

Use High Resolution Data to Create "Decision Units" for Treatment Dosing

DEPTH

Injection Depth	Area A 500 sq. ft, 5 pts.	Area B 1,500 sq. ft, 15 pts	Area C 4,000 sq. ft. 40 pts.
12'			
14'	10 lbs	25 lbs	10 lbs
16'	40 lbs	40 lbs	25 lbs
18'	25 lbs	25 lbs	25 lbs
20'	10 lbs	10 lbs	10 lbs
22'			10 lbs

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BOS 200®

- **Carbon/Biological Based Product Made of:**
  - Activated Carbon
  - Calcium Sulfate
  - Nitrate
  - Micro and Macro Nutrients
- **The Trap and Treat Mechanism:**
  1. **The "Trap": Activated carbon adsorbs hydrocarbons.**
  2. **The "Treat": In place biodegradation of the HC**

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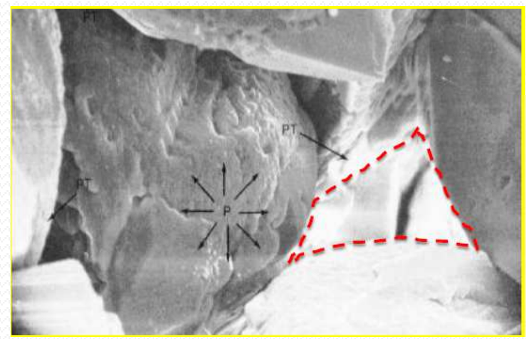
Powdered Activated Carbon

“My Old Friend” (Tom Fox, CDLE-OPS, LUST-Line)

- **Sourced from coal, wood, or nut shells.**
- **Activation process increases surface area by creating pores in a carbon matrix.**
- **One pound has ~100 acres surface area.**
- **Apparent density ~0.5 g/cc (30 lbs/cu ft).**

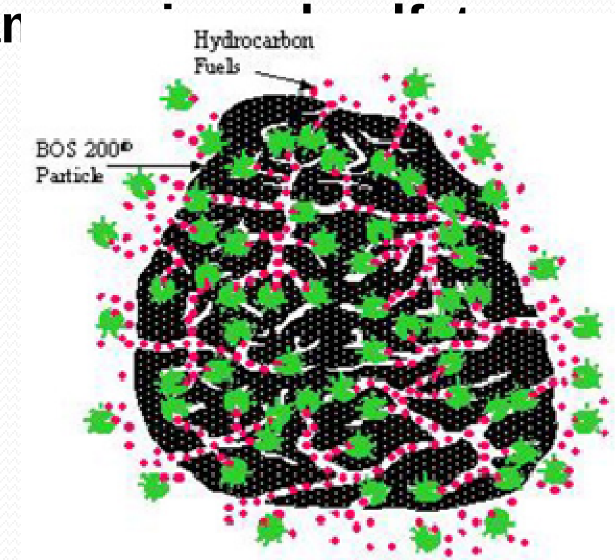


- **Absorbs 10-35% of its weight in hydrocarbons.**
- **Indefinite retention of contaminants.**
- **Inhalation hazard, but non-toxic if ingested.**

BOS 200®

- Inventor – Scott Noland, President - RPI
- Ideal environment for the biological process, where hydrocarbons are adsorbed on to BOS 200® particles made up of:
  - Electron Acceptors: oxygen, nitrate, ar
  - Nutrients - phosphorus and nitrogen
  - Aerobic and Anaerobic Blend of Microbes
  - Initially, Aerobic but then Anaerobic

    (Oxidation to Sulfate Reduction)



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Mixing / Inoculation

- Mixing

  Some Chemistry Takes Place

  1. Nitrogen and Phosphorus Two Main Requirements
  2. Dissolution of Nutrients
  3. PPT of Calcium Phosphate for Long-Term Source
  4. Saturation with Oxygen

- Inoculation
  - Providing Time for Organisms to Inhabit the Pore Structure

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Aerobic

- One of the Most Energetically Favorable Paths
- End Products = CO_2 and Water
- Along the Way Catechols, Alcohols, Aldehydes, Ketones, and VFA's are Produced.

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Anaerobic

- **Denitrification**

  $NO_3^- \Rightarrow NO_2^- \Rightarrow NO \Rightarrow N_2O \Rightarrow NH_4 \Rightarrow N_2$

- **Sulfate Reduction**

  $SO_4^{2-} + HC \Rightarrow CO_2 + H_2S + H_2O$

- **Multivalent Metals** (Fe, Mn, primarily)

- **Fermentation**

  $C_6H_{12}O_6$ + 2ADP + 2 phosphate $\Rightarrow$ 2 Lactic Acid + 2 ATP

  (many paths: C3, C4, acetogenesis, mixed acid, etc)

- **Methanogenesis**

  $C_6H_6 + H_2O \Rightarrow CH_3COOH + H_2$

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Blend of Microorganisms

- At Last Count Approx. 27 Organisms
- Byproducts Nearly Impossible to Predict
- One Bugs Waste Another's Desert
- Sulfide Controlled by Oxidation
- Capable of Degrading BTEX, Ethers, Alcohols, 1,4-Dioxane, THF, and a host of other HC's
- Greater Than the Sum of the Individuals

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The Bugs are Too Big

- Can Inhabit the Macro and Meso Pore Structure
- Larger Pores Primarily Used to Transport not Adsorb
- Bugs Prefer Surfaces – Attach and Create Biofilm
- Secrete Enzymes to Facilitate Food Intake

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LNAPL

- Pores Saturated with Water
- LNAPL is Hydrophobic
- Cannot Overcome Osmotic Pore Pressure to Displace Water
- Can Sorb to Surface
- Surface Diffusion Promotes Bioavailablity

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Kinetics of BOS 200

- First Order Kinetics
  1. Rate of Change of Concentration with Time is Proportional to the Concentration.
  2. $Ln(C/C^{o}) = -kT$
- Which Concentration is Important?

  GW – Soil – BOS 200
- Rates of Degradation Can be Very High

Detecting Activity

- Pre & Post Injection Sampling for Changes in:
  - Anions
  - VOCs (BTEX, TPH, Other HC)
  - Gases (methane, CO_2)

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Applying RDC Data to In Situ Remediation Treatments

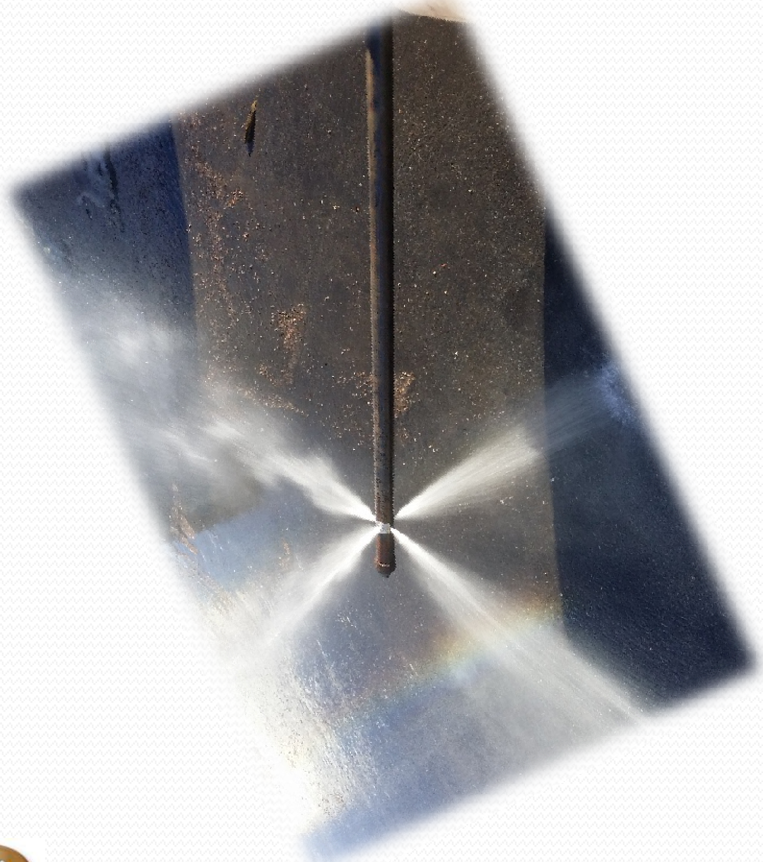
- **Now we know *where* the contaminants are and *how much* is there, so now we need *properly targeted & applied treatments*.**
- **Old vs. New Application Methods**
- **Conventional Injections vs. Hydraulic Fracturing Methods**

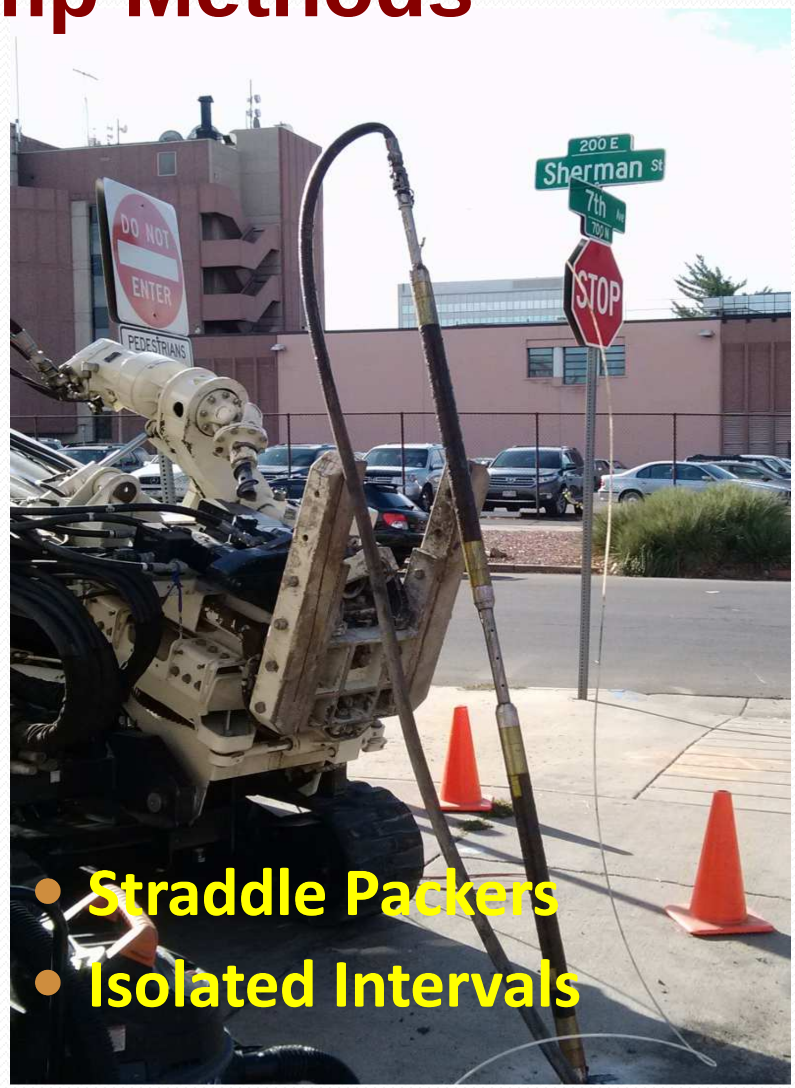
The "Old" Ways:
Bottom Up Injecti

- Path of Least Resistanc
- Less Porous & Perme
  Soils
- Preferential Beddin
  Planes
- Fracturing May Occu
- Coarsening Downward

SOLUTION:
Improved Tools & Pump Methods

- Top-Down Injections Tools
- High Pressure, High Flow

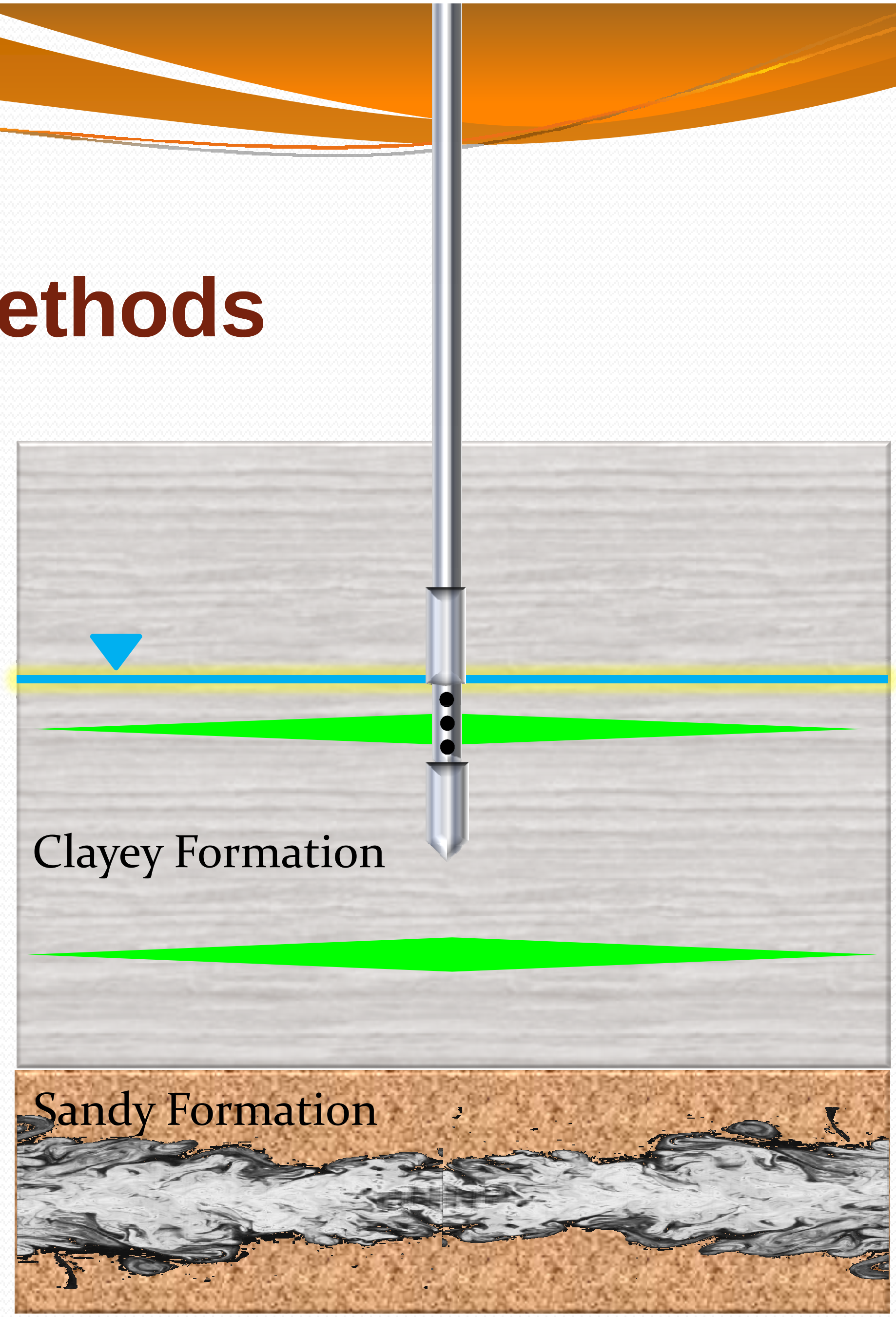




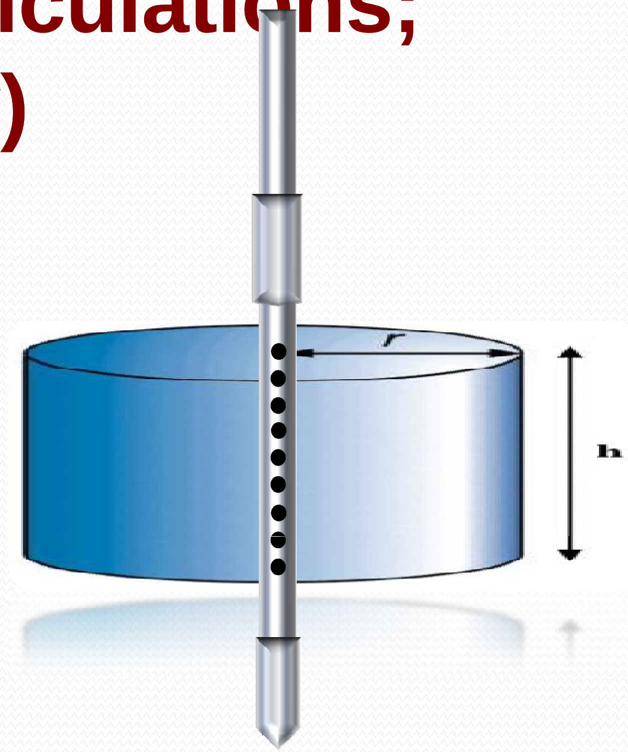
- Straddle Packers
- Isolated Intervals

SOLUTIONS:
Improved Injection Methods

- Top Down Injections
- Lateral Inj. Ports or Packers
- High Pressure/Flow
- Precise Placement
- Low Perm will Fracture
- Permeable Zones will Fluidize
- *= BETTER CONTACT!*



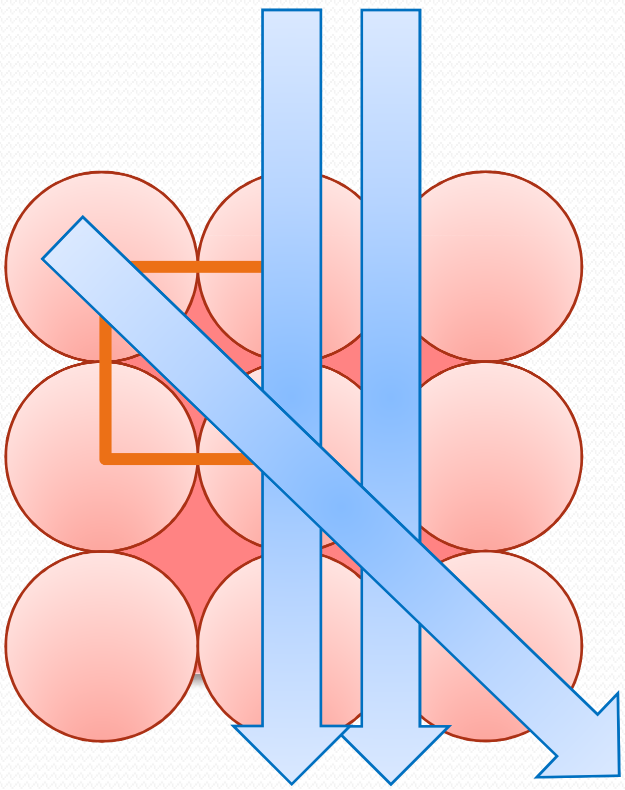
Radius of Influence (ROI) Calculations; (Displacement vs. Pore Flow)



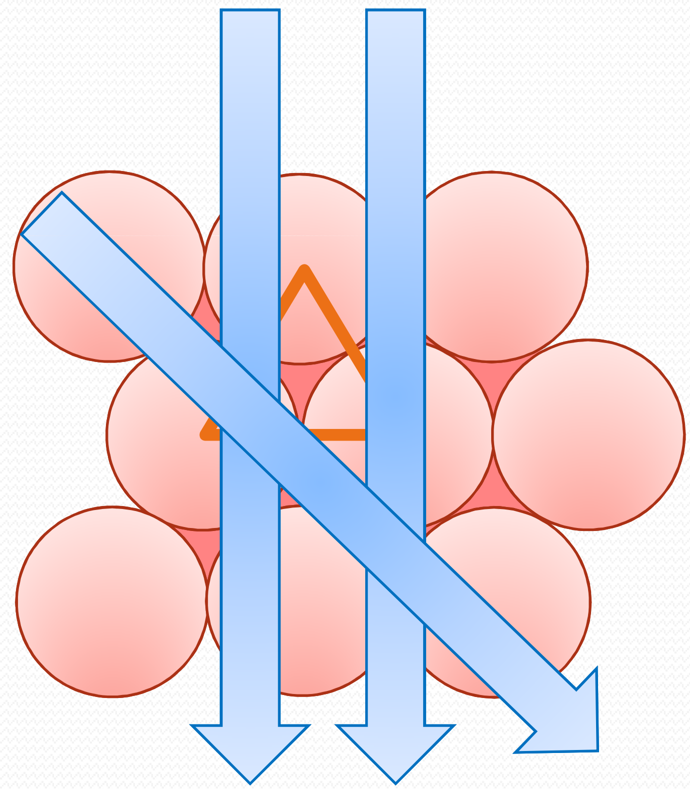
- **10' Injection Grid:**
  - **Radius = r = 5'**
  - **Area = πr^2**
  - **Vertical Treatment Interval = h = 2'**
  - **Assuming *Effective* Porosity ≈ 20%**
  - **Volume conversion: 1 ft^3 = 7.48 gallons**
- **Therefore:**
  - **Volume = $\pi(5')^2$ x (2') x (0.2) = 31.42 ft^3**
  - **Pore volume = 31.42 x 7.48 = 235 gallons**
  - **A 50 gallons injection = about 21% of pore volume.**
- **HOWEVER: ROI is more a function of what % of the formation fractures during injection (displacement) vs. pore space flow.**
- **Do a Pilot Test Injection Phase with Confirmation Cores.**

Triangular vs. Square Injection Grids
(Surface View)

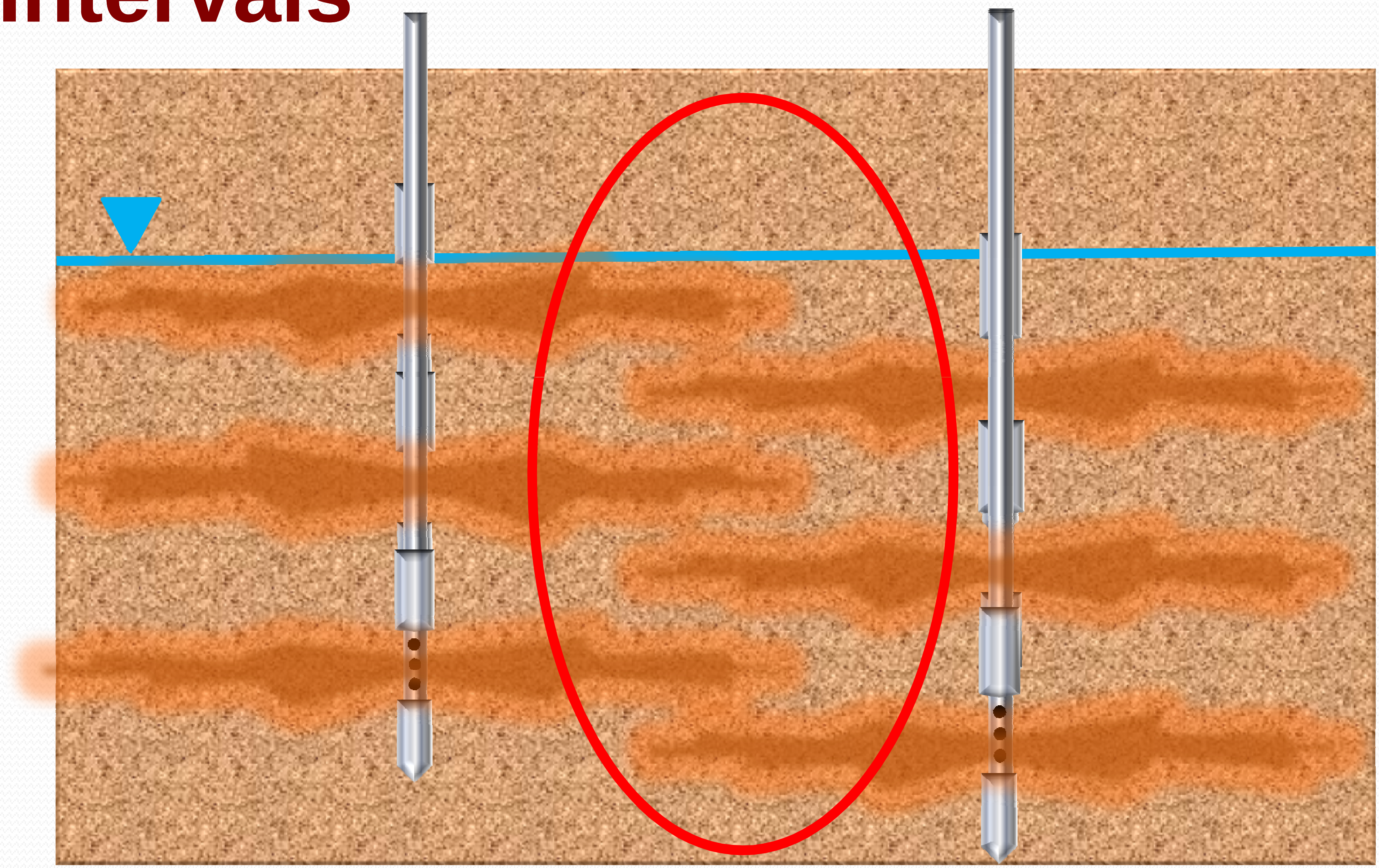
- **Square Grid**



- **Triangular Grid**



Staggered Top-Down Injection Intervals



Slurry (Powders & Solids)
Specialized Mixing & Pumping Systems

CLEAN INJECT

Performance Monitoring

- **Post Injection Core Observations – Spacing Confirmation**
- **Samples Monitor Wells Before and After Injections**
- **Monitor Water Levels During Injections, Observe for Impacts**
- **Clean Out Impacted Wells**
- **Collect Valid Water Samples Post Injection**
  - **Weekly to Monthly right after injections for 3 Months**
  - **Quarterly Thereafter**
  - **BETX, TPH, Selected Anions**

Detecting Activity

- Pre & Post Injection Sampling for Changes in:
  - Anions
  - VOCs (BTEX, TPH, Other HC)
  - Gases (methane, CO_2)

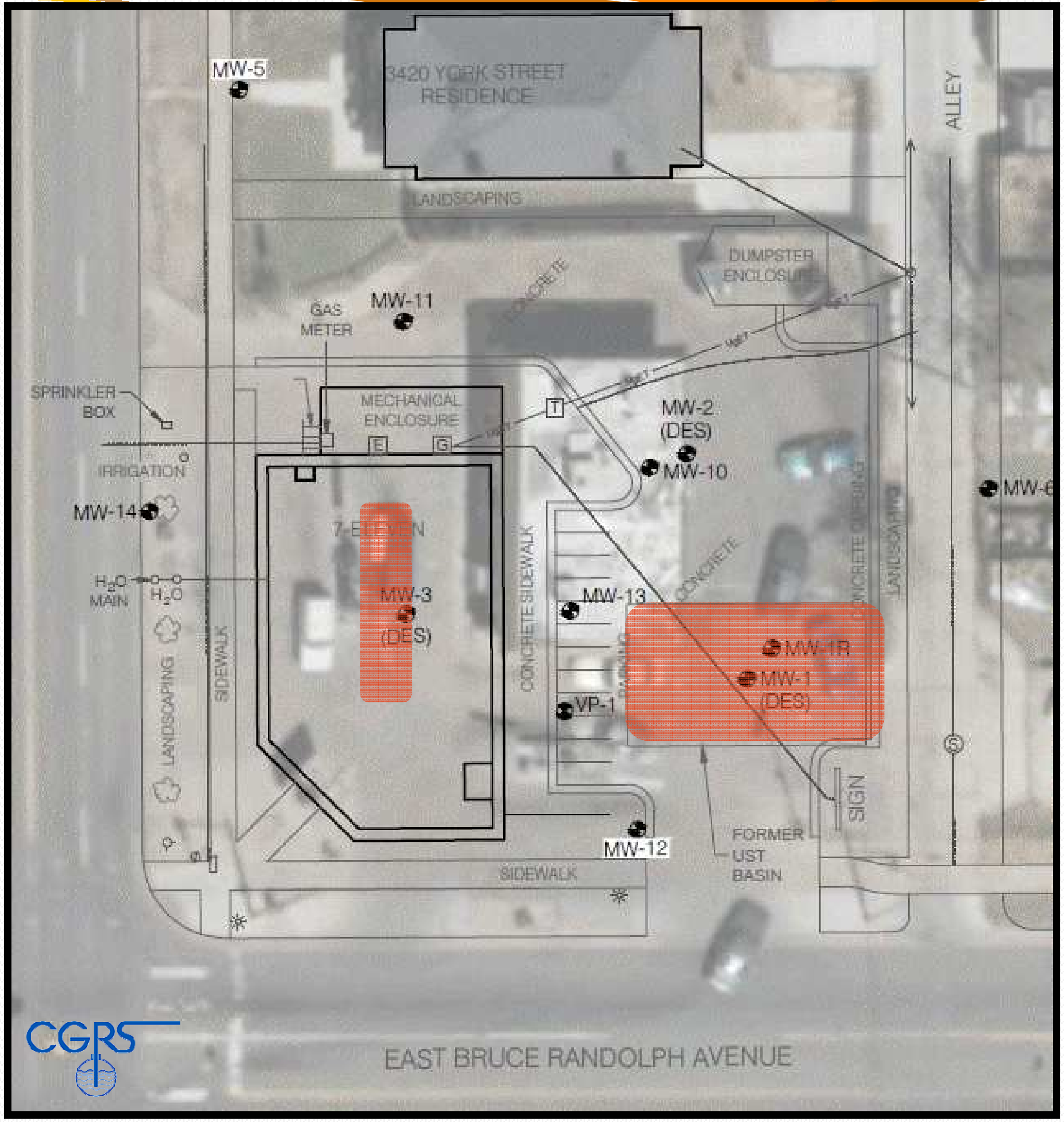
Ex. #1: 3400 York Street; Denver, Former Gas Station

- **CDLE-OPS Event No. 11494**
- **Release Discovered During Tank System Removal, August 2011**
- **2nd Tank System Removed July 26, 2012; No Release Detected.**
- **Co-Mingled with PCE Plume from Upgradient Dry Cleaner Site**
- **New 7-Eleven Store Built Over Part of Plume Prior to Remediation**
- **Relatively Deep (Groundwater at ~45')**
- **Site Consultant:** CGRS

3400 York Street; Phases of Work

- **Site Developer: "NOT WAITING," New Building Going In Before Injections Started.**
- **Chosen Remedy: RPI BOS-200®** (Activated Carbon, Nutrients, Bacteria Augmentation)
- **The Plan:**
  1. **RDC Sampling & Treatment Design**
  2. **Pilot Injection Test Conducted Near MW-1R, Former Tank Pit Area** (May 2013)
  3. **Full Scale Site Injection on Balance of Site** (Nov. 2013)
  4. **Post Injection Well Cleaning and Redevelopment**
  5. **Post Injection Sampling & Monitoring**

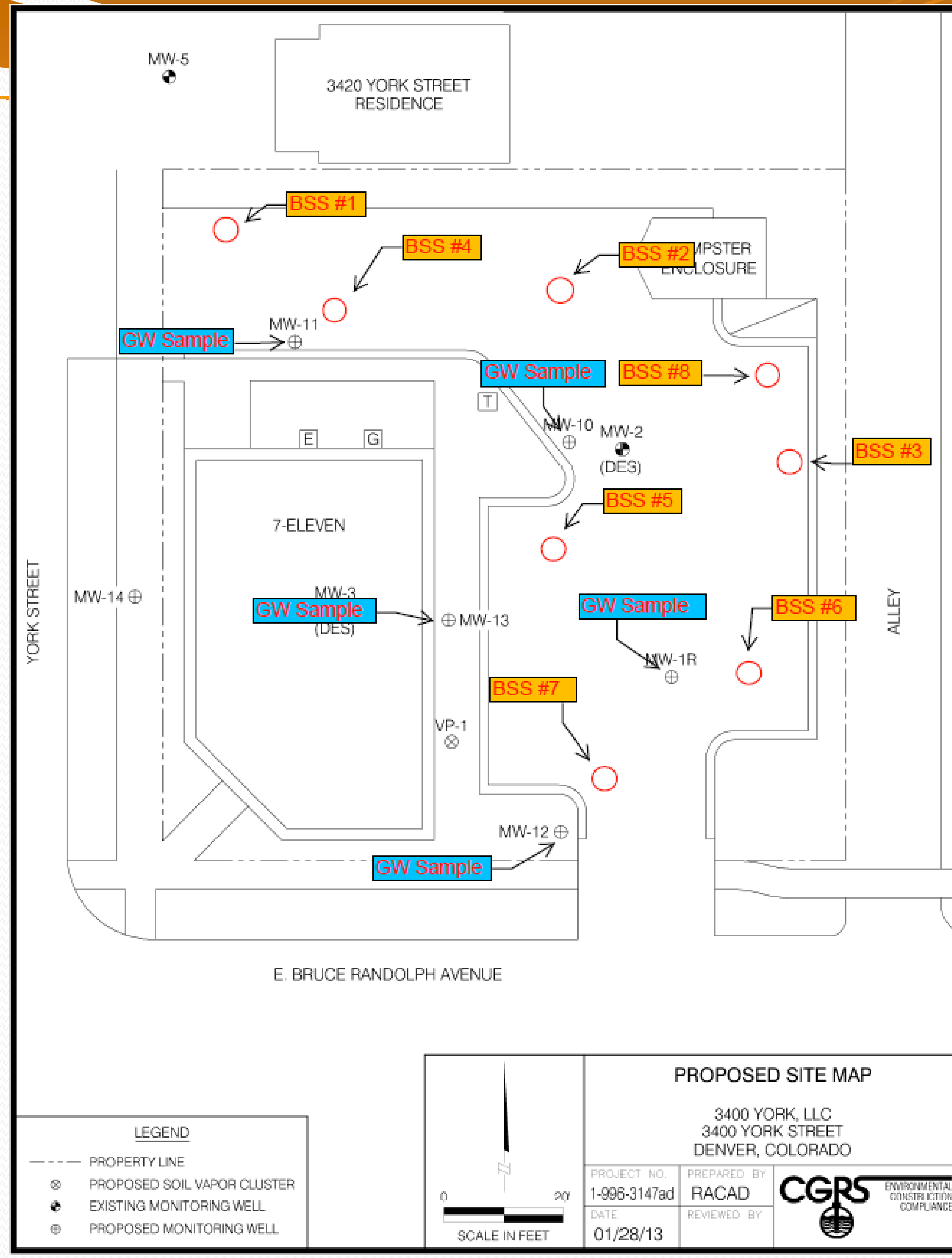
Overlay of New Building Plan on Former Gas Station Site



Courtesy CGRS Inc.

RDC Event

- **8 Continuous Soil Cores 5' – 50' in Treatment Area**
  - 56 soil samples collected at 2' composite intervals.
- **5 Monitor Wells Sampled in Treatment Area.**
- **Analysis of 56 Soil & 5 Ground Water Samples:**
  - 8260 VOCs (BTEX, MTBE, TVPH, PCE & Daughters)
  - Sulfate, Chloride, Nitrate, Nitrite, Acetate (waters only)
- **Identified Shallow Vadose Contamination in Former Tank Pit Area.**



Courtesy CGRS Inc.

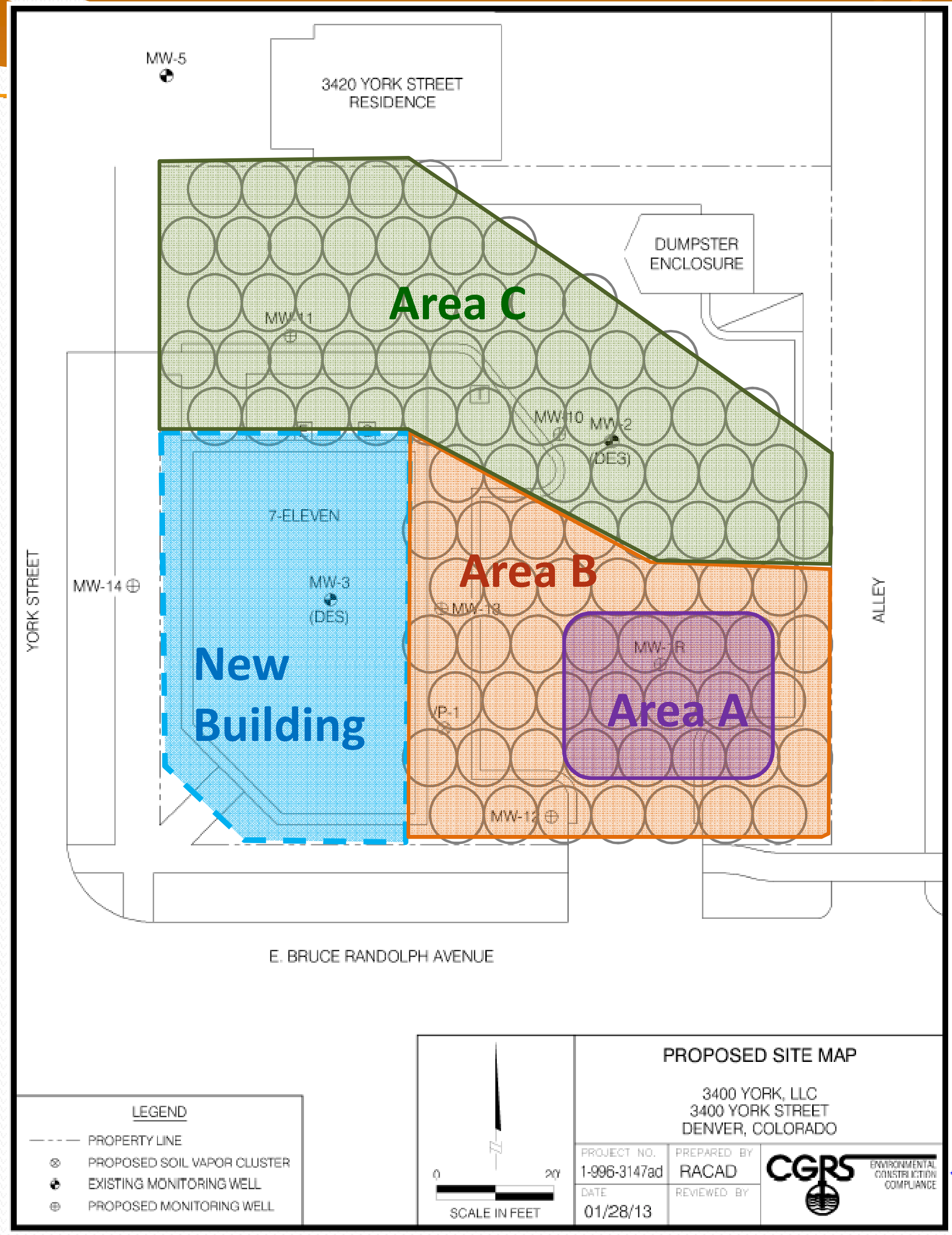
Injection Design

PILOT TEST: (May 2013)

- **Area A:** MW-1R, former tank pit/source area; 12 pts, 15lbs/ft. 40'-50'
- **Total** 1,800 lbs BOS200

FULL SCALE: (Nov 2013)

- **Area B1:** 15pts, 10 lbs/ft, 40'-50'
- **Area B2:** 16 pts, 7.5 lbs/ft, 40-50'
- **Area C**: 42 pts, 5 lbs/ft, 40-50'
- **Total** 4,650 lbs BOS200



Courtesy CGRS Inc.

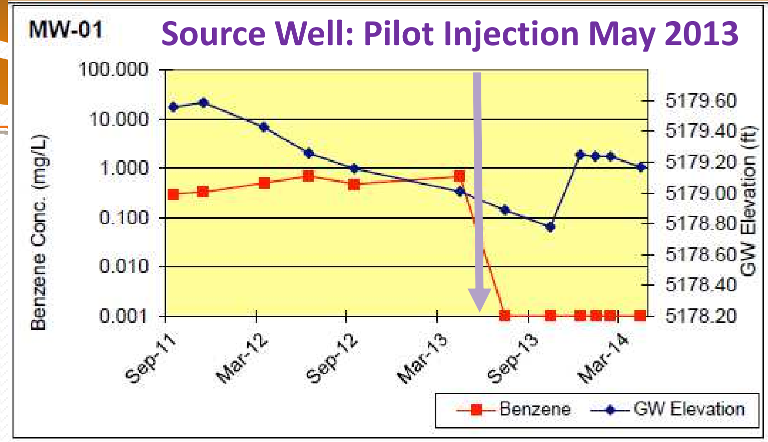
Results (Benzene ppb)

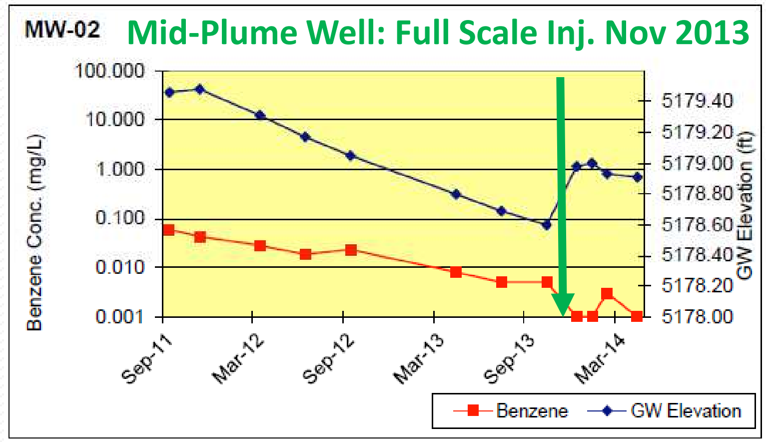
SOURCE:

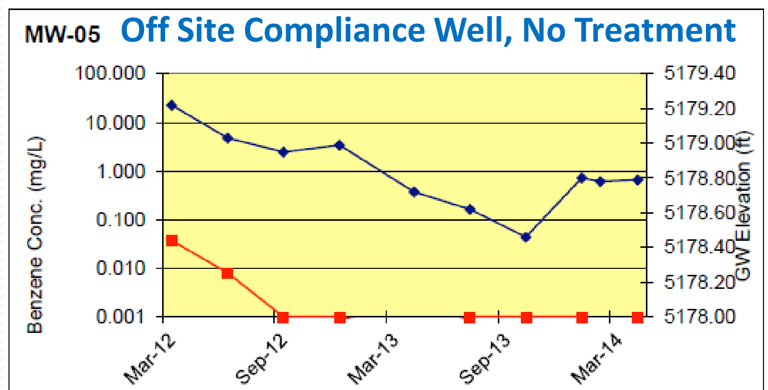
- **MW-1R:** 310-688 ➔ ND
  - (PCE: 3330 ➔ ND)

MIDPLUME:

- **MW-10/2:** 8-60 ➔ ND-3
  - (PCE: 6270 ➔1830)
- **MW-11:** 2-3 ➔ ND
  - (PCE: 2710 ➔ 11)
- **MW-12:** 5-12 ➔ ND-3
  - (PCE: 13900 ➔12900)
- **MW-13**: 23-47 ➔ 3-6
  - (PCE: 595 ➔ 1080)
- ***NFA** achieved in 2015 after 6 post injection monitoring events*







Courtesy CGRS Inc.

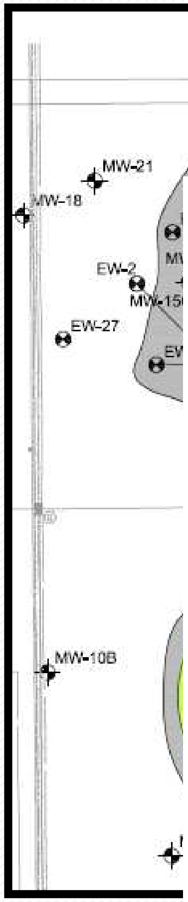
Cost to Our Client (Labor & Materials)

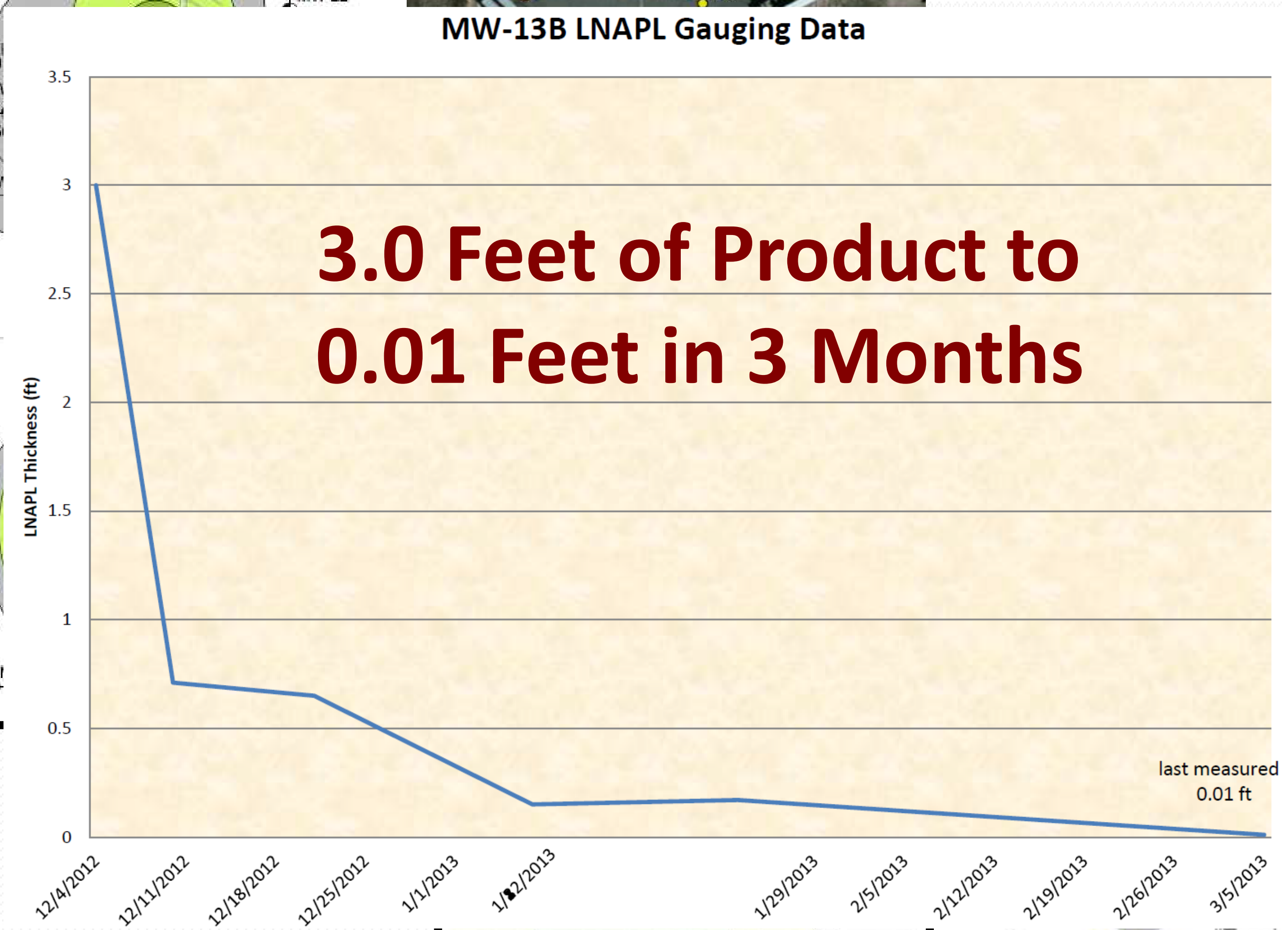
• RDC Sampling	• $5,000
• Pilot Test	• $16,000
• Full Scale	• $57,000
• **TOTAL:**	• **$78,000**

= Cost Effective Cleanup – The First Time!!

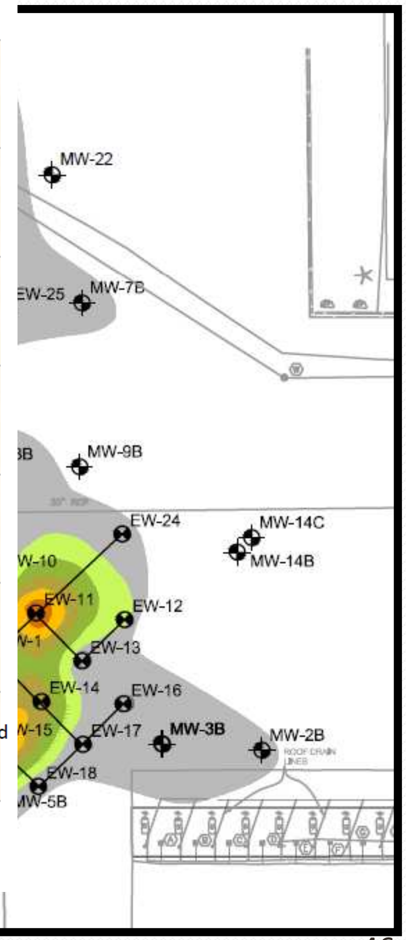
Yes – LNAPL Too!

- Busy Truck Stop
- Pilot Test
- Removed NAPL @ MW-13B





3.0 Feet of Product to 0.01 Feet in 3 Months

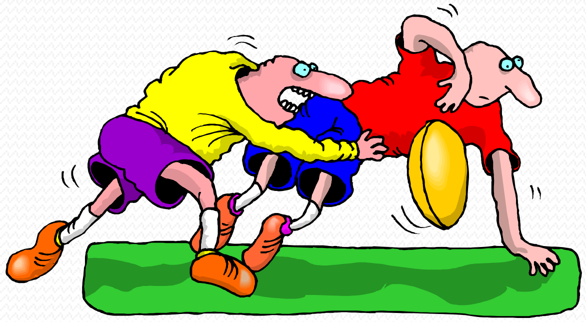
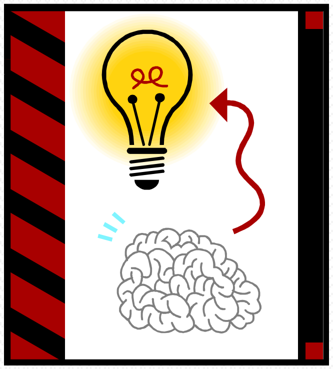


Summary

- **In-Situ Treatment Success Rates are Significantly Improved by:**
  - **Performing a RDC phase to create a 3-D CSM by utilizing:**
    - **3-D Imaging (Qualitative)**
    - **High Resolution Sampling Tools (Quantitative)**
  - **Advanced Targeting Injection Tools and Methods**
  - **Design Using Decision Units -Targeted Dosing**
  - **Understanding ROI and Hydraulic Fracturing**
  - **Utilizing Pilot Testing, Performance Monitoring Tools, Monitoring Progress and Make Adjustments on the Fly.**
- ***The Goal of Clean Up & Closure – The First Time Around!***

More Summary

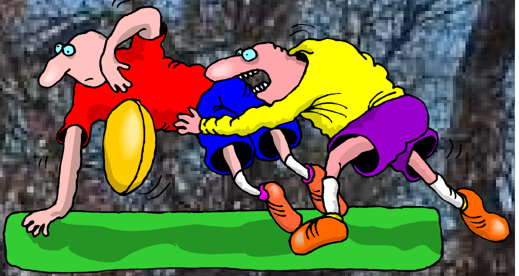
- *It's a Contact Sport, AND A TEAM SPORT !*


- *Geology, Hydrology, Chemistry, Biology*
- *Consultant + Driller + Installer + Supplier*




Questions?



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