Department of the Environment

Emerging Technologies for Site Characterization and Remediation for Petroleum Hydrocarbons

18th Annual Maryland Ground Water Symposium

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MDE Oil Control Program

Presentation Outline

- **Improved Site Characterization – Direct Push Enhancements**: Resistance, Hydraulic, MIP, LIF logging
- **Emerging Technologies:** Surfactant Soak/EFR; Chemical Oxidation; Oxygen Releasing Compounds; Oxygen Addition Technologies; Above Ground Bioreactors; Recirculating wells; Permeable Reactive Barriers; Phytoremediation
- **Other Factors:** Time Frame, Receptor, Cleanup Endpoints

Enhancements to Direct Push Technologies for Improved Site Characterization

- Resistance Logging – Characterizes lithology changes by measuring formation resistance
- Hydraulic Parameter Testing – Determines permeability and ability of formation to accept remedial injections by injecting water at different zones
- Membrane Interface Probe (MIP) – Provides discrete interval analysis of dissolved phase constituents
- Laser Induced Fluorescence (LIF) – Provides discrete interval analysis of liquid phase hydrocarbons (LPH)

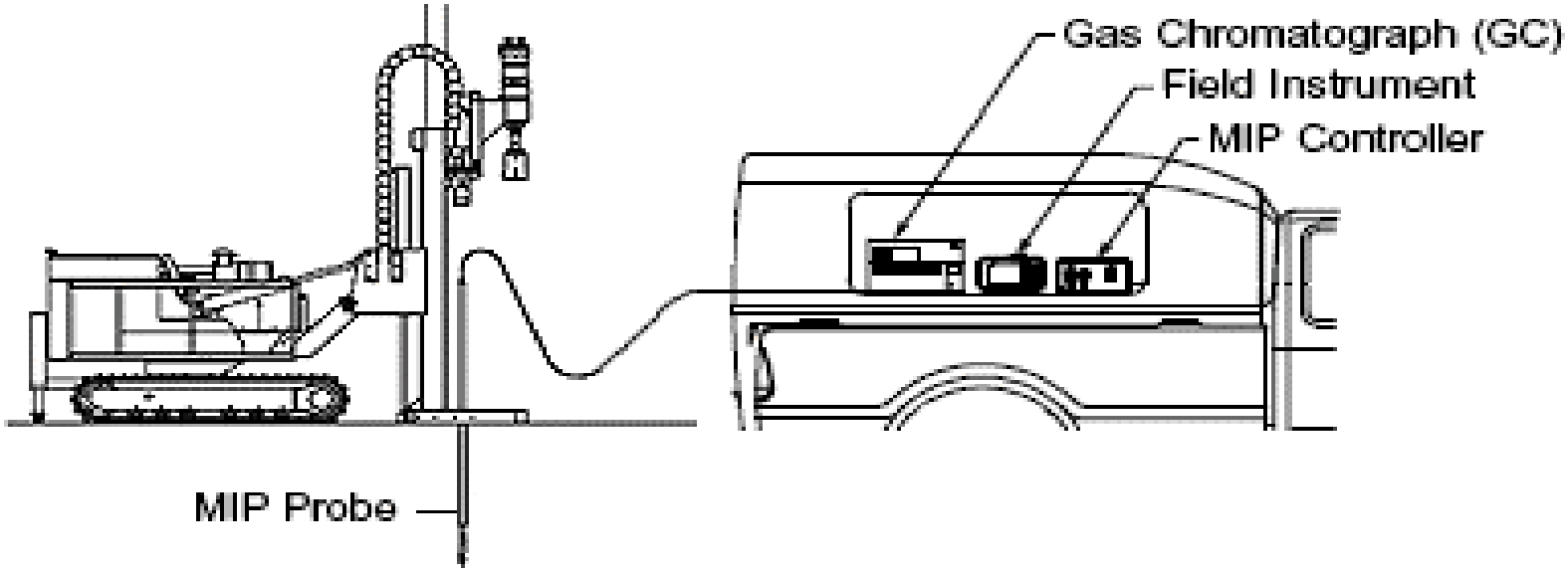
Direct Push Enhancements (cont.)

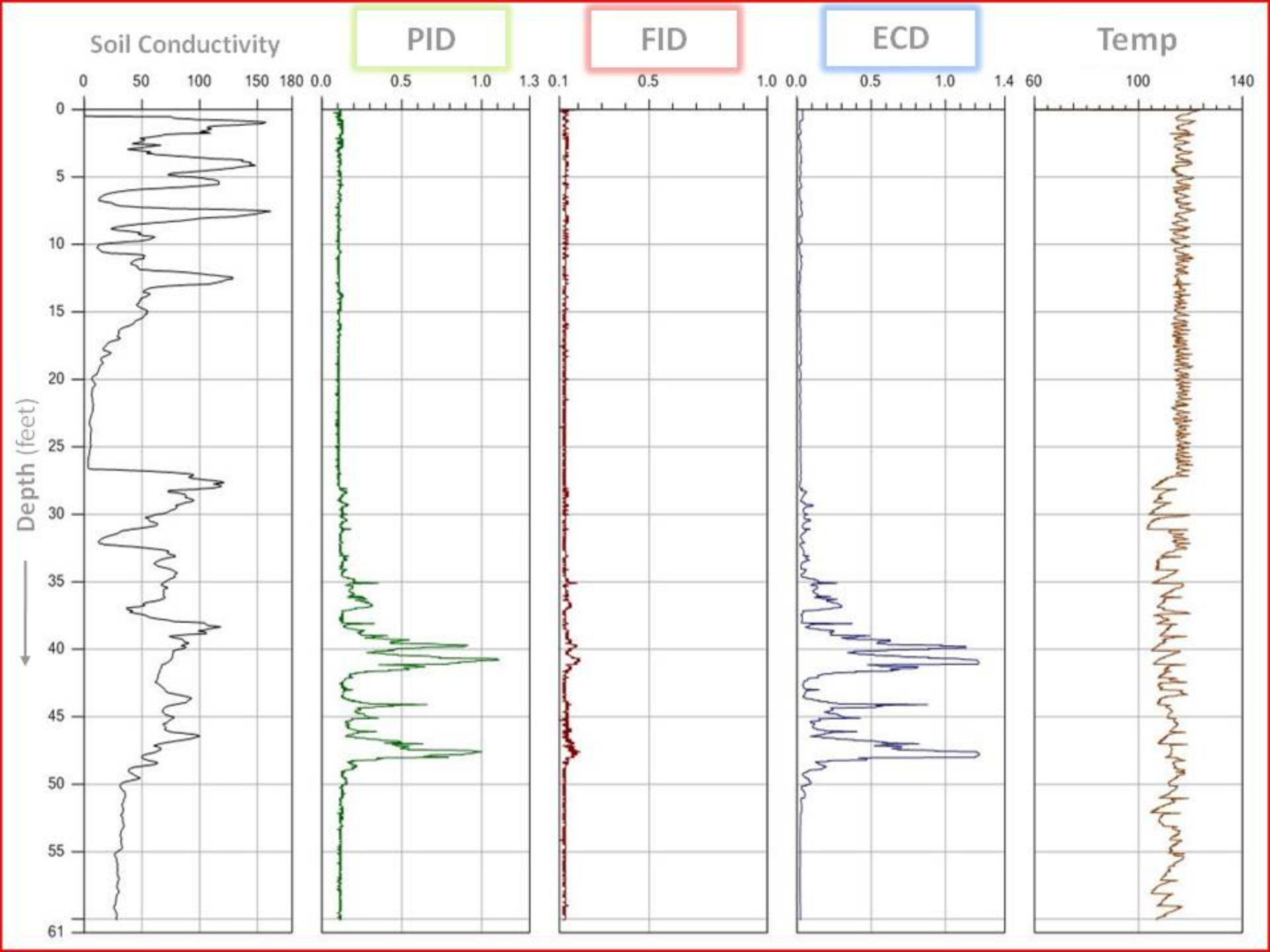
- Real time instrument responses stored on field computer for review
- 3-D processing software produces graphics that can be sent to a website for review that evening to direct the next days field work
- Confirmatory borings and sampling conducted to verify instrument responses

Direct Push Enhancements (cont.)

- Use 3D data to select locations for:
  - Additional monitoring wells
  - Injection locations and depth intervals for remedial treatments
  - Follow up survey can be used to determine treatment effectiveness

Direct Push – Rig Setup




Soil Conductivity
PID
FID
ECD
Temp
0
50
100
150
180
0.0
0.5
1.0
1.3
0.1
0.5
1.0
0.0
0.5
1.0
1.4
60
100
140
Depth (feet)
0
5
10
15
20
25
30
35
40
45
50
55
61

ECD Response >3.5E+005uV
Relative Azimuth = 270°, Elevation = 0°, Z Exaggeration = 2.00
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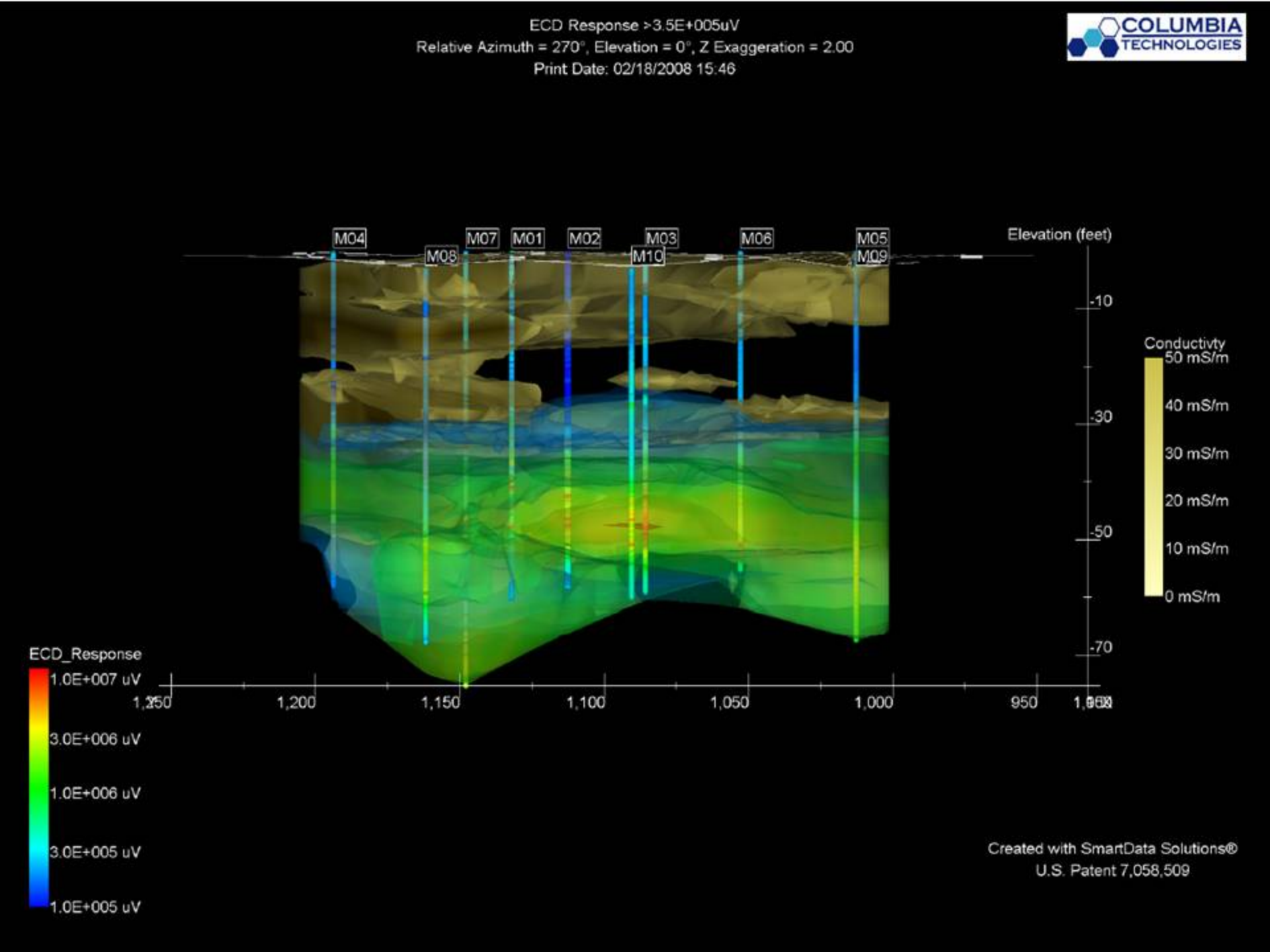


Overview of Technologies to be Discussed

- Surfactant Soak / EFR
- Chemical Oxidation
- Oxygen Releasing Compounds
- Oxygen Addition Technologies
- Above Ground Bioreactors
- Recirculating Wells
- Permeable Reactive Barriers
- Phytoremediation

Other Factors in Technology Selection

- **Time Frame** – Passive technologies may be slower than injection technologies
- **Receptor** – High risk may require shorter time frame and lower cleanup endpoints
- **Endpoint** – Lower cleanup endpoint may require polishing technologies
- Initial LPH recovery usually requires aggressive hydraulic and vapor capture; technologies discussed today are usually the next step after diminishing returns reached with aggressive technology.

Cleanup Endpoints

- **Mobile LPH** – LPH plume is not stable, need hydraulic and vapor control
- **Residual LPH** – LPH plume is stable, levels down to a few inches to a reoccurring sheen
- **High Groundwater Concentrations** – dissolved levels 1,000s ppb near source, causing down gradient impacts
- **Low Groundwater Concentrations** – dissolved levels 100s ppb, down gradient receptors, need for lower cleanup endpoints

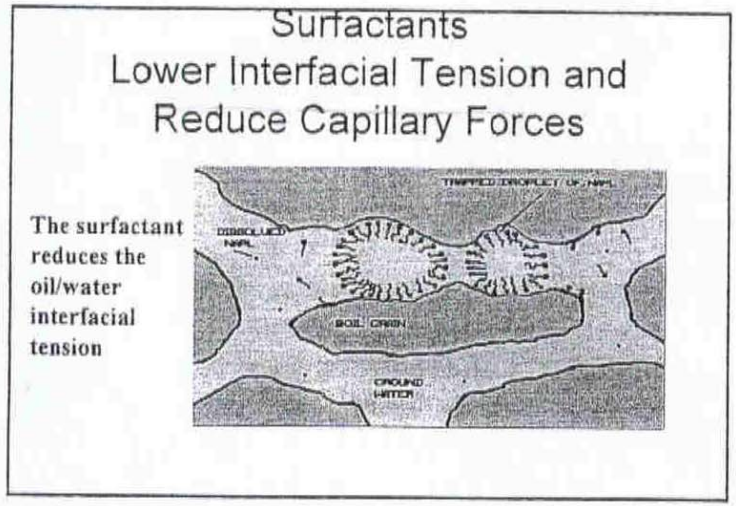
Surfactant Soak / EFR

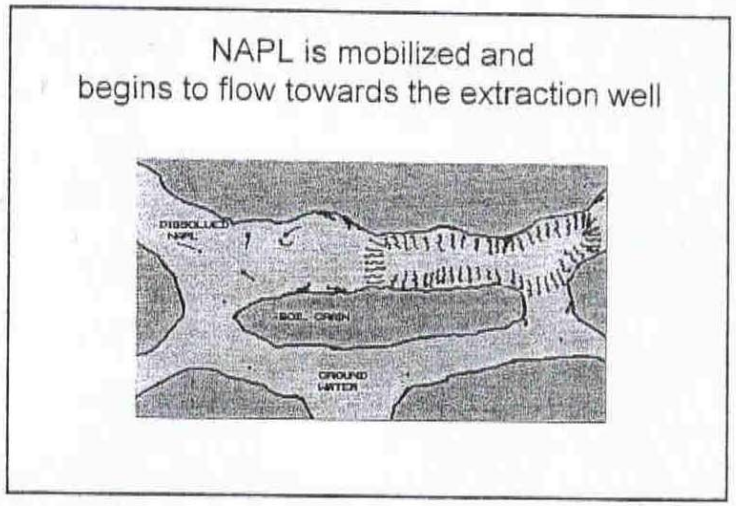
- Used to remove Residual LPH from the formation
- LPH is trapped by capillary forces/interfacial tension in formation
- Surfactants lower interfacial tension and reduce capillary forces
- LPH is mobilized and can be drawn into the extraction well(s)
- Concerns – soap bubbles in sensitive receptors such as surface water bodies, drinking water wells

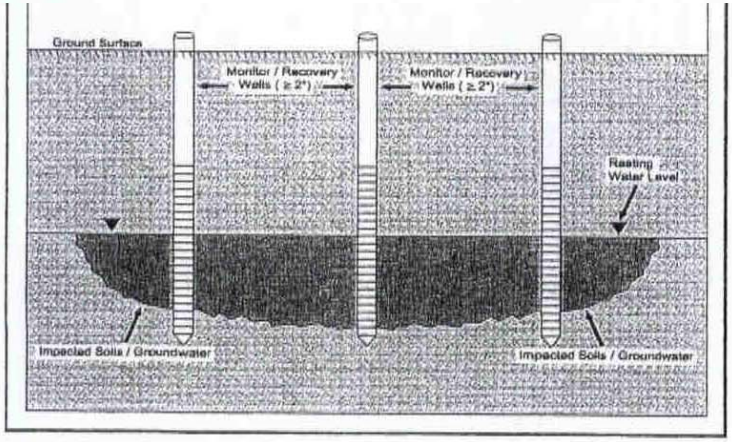
Surfactant Soak / EFR (cont.)

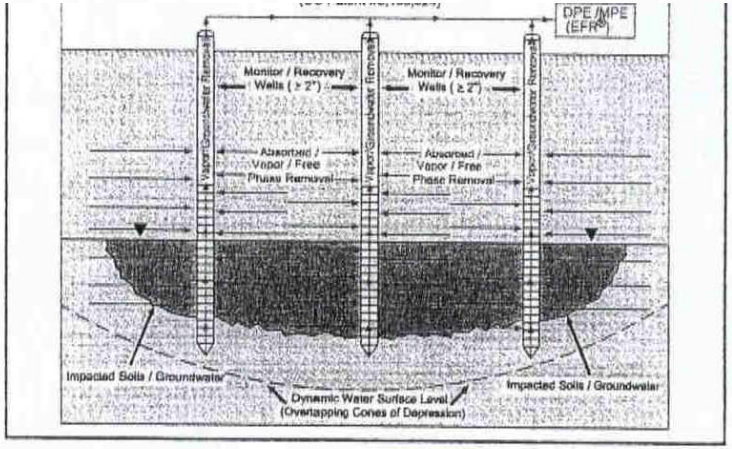
- Surfactants injected – not high pressure, need a high volume flood to draw surfactants through the source area
- 1-2 days contact time before EFR or pump and treat
- Need to understand site hydrogeology, EFR capture zone and area of mobilization
- ECOVAC ™ approach – multiple wells drawn down with vac truck, expose smear zone then add surfactants

Surfactant Soak/EFR – Ecovac™ Approach









Chemical Oxidation

- Chemical stability of commonly used oxidants – persistence after injection
  - Typically use catalyzed sodium persulfate in Maryland, persists weeks to months. Some problems with hydrogen peroxide/Fenton-short persistence, hard to control, violent reactions
    - Other oxidants sometimes used – permanganates, etc.

Chemox (cont.)

- Chemox applicability – Ideally used to remediate high and low level dissolved phase plume
- Advantages – focus on remaining hot spot, relatively inexpensive, reactions destroy plume
- Disadvantages – may require multiple applications, vapor migration, mobilizes plume
- Concerns – bench and pilot studies to determine soil oxygen demand, treatability, and safe handling of oxidants.

Chemox (cont.)

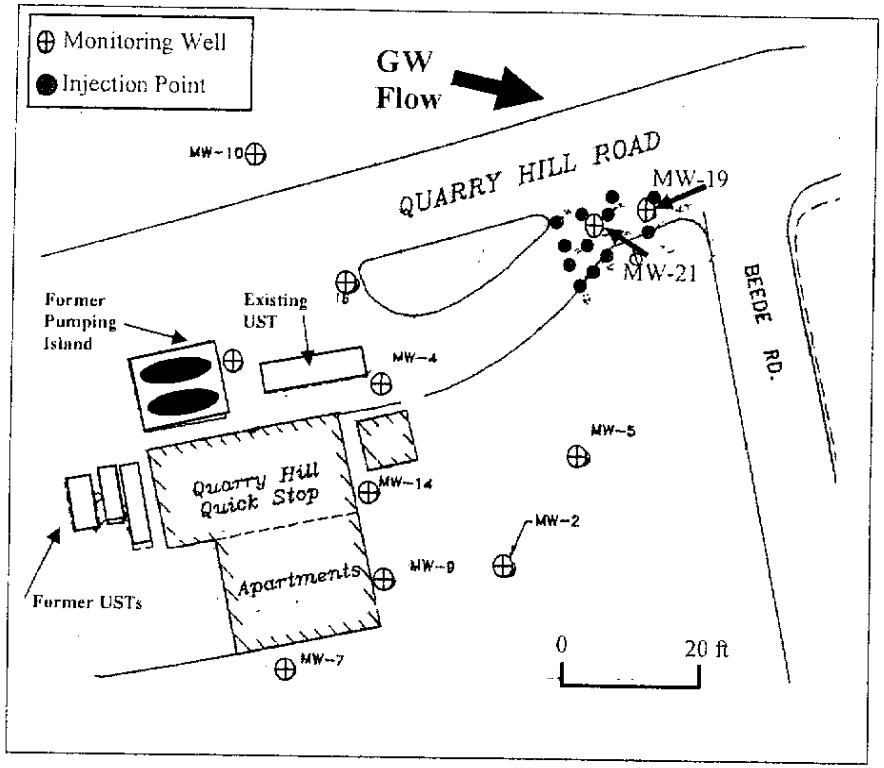
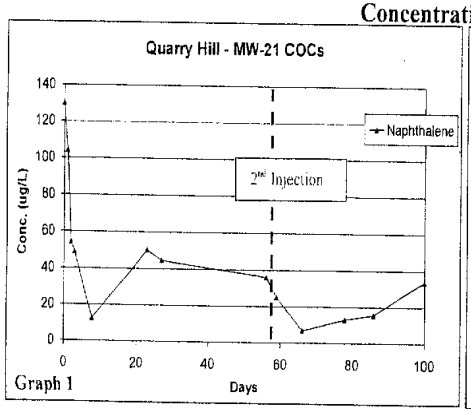
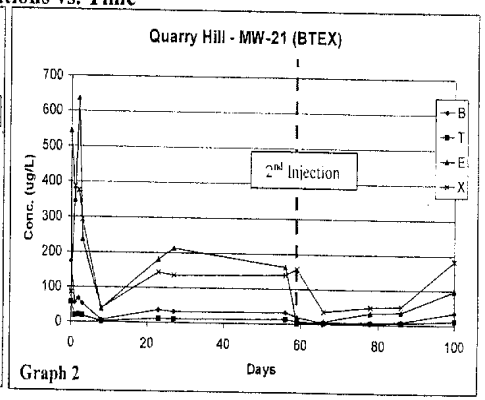


Figure 1. Site Map with RegenOx Injection points around well MW-19 and MW-21

RESULTS

Concentrations vs. Time

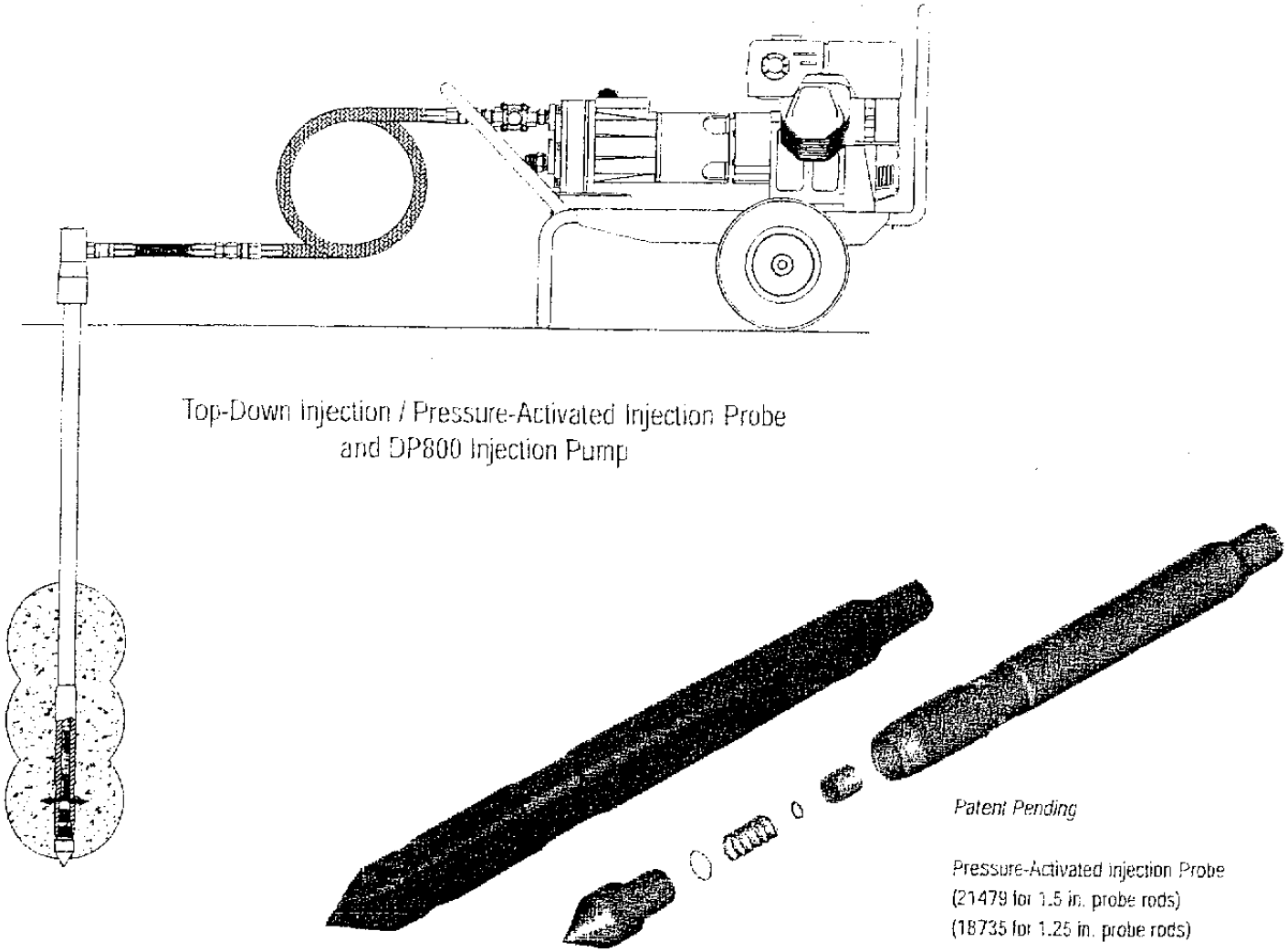




Chemox (cont.)

- Why direct push for materials injection? (chemox and ORC)
  - Compact machines
  - Precise targeting of the treatment zone
  - Low site impact
  - Cost efficient
  - Replicability from pilot test to full scale implementation

Chemox (cont.)


Top-Down Injection / Pressure-Activated Injection Probe
and DP800 Injection Pump
Patent Pending
Pressure-Activated Injection Probe
(21479 for 1.5 in. probe rods)
(18735 for 1.25 in. probe rods)

Oxygen Releasing Compound Injections

- Used to polish moderate and low level dissolved phase contaminant plumes
- Petroleum hydrocarbon degradation has been shown to be most limited in the formation by the presence of oxygen
- Adding a compound (calcium hydroxide) that slowly releases oxygen increases available oxygen for biodegradation

ORC Injections (cont.)

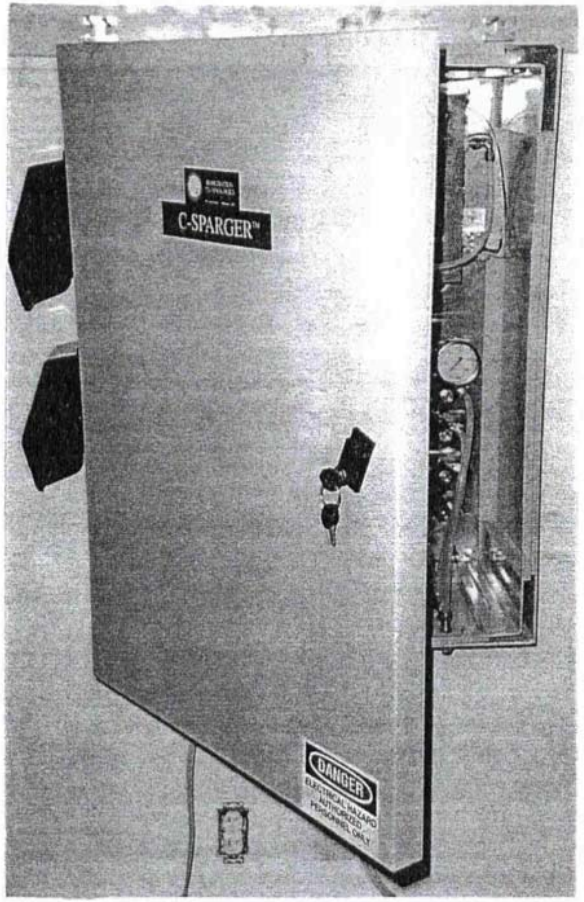
- Typically grid injections in source area with a direct push rig, similar to chemox
- Typical radius of influence (ROI) is about 15 feet
- Site specific ROI should be determined in pilot study
- Polishing technology for a dissolved plume in a favorable formation
- Must have enough oxygen to address remaining mass of dissolved plume
- New products (Regenox™) combine chemox with a later timed release of ORC to finish polishing through biodegradation

Oxygen Addition Technologies

- KVA™ Microbubble / Ozone Spargers
- ISOC™
- Used to polish high and low level dissolved phase contaminant plumes
- Concerns
  - Limited ROI, passive, so limited in tight formations, more expensive way to introduce oxygen than SVE/sparge
  - Well biofouling in some groundwater geochemistries

KVA™ Microbubble / Ozone Sparger

- Oxygen normally limited to 7 mg/l
- Can supersaturate up to 35 to 100 mg/l and increase mass of oxygen in groundwater
- Specially designed diffuser and oxygen delivery system performs supersaturation



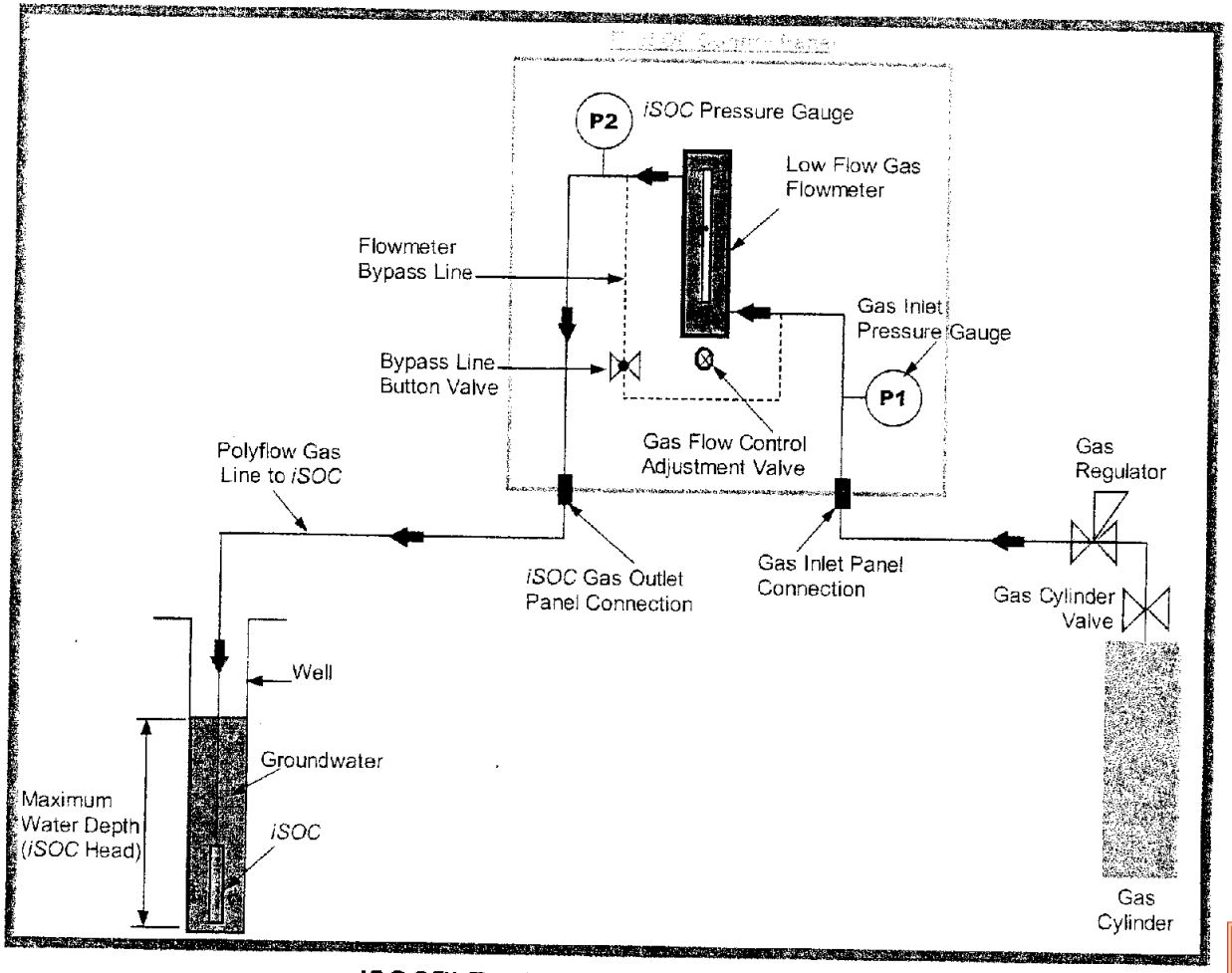
The C-Sparger® System

ISOC™ Diffuser

- Different diffuser design than KVA™
- Simpler, more common in Maryland than KVA™
- Can create a down gradient oxygen curtain in multiple wells

Layout of ISOC™ System

What does an *iSOC*™ System Look Like?



***iSOC*™ Equipment Setup Schematic**

Bioremediation

Bioremediation

- Types of bioremediation
  - Engineered in-situ fluids-injection, recirculation, or permeable barriers
  - Monitored natural attenuation, land farming
  - Recent focus on above ground bioreactors in fractured rock remediation
  - Concerns
    - Knowledge of fracture depths and orientation and wells intersecting fractures

Bioremediation

- Elements needed for bioremediation
  - Knowledge of site groundwater geochemistry
  - Macronutrients – N, P, K, S (fertilizer)
  - Micronutrients – Mn, Fe, Zn, Bo, Cu
  - Oxygen source
  - Bacterial consortium – can be use of “bugs” in native formation or added
  - Enzymes – mimicking naturally produced microbial extra cellular enzymes

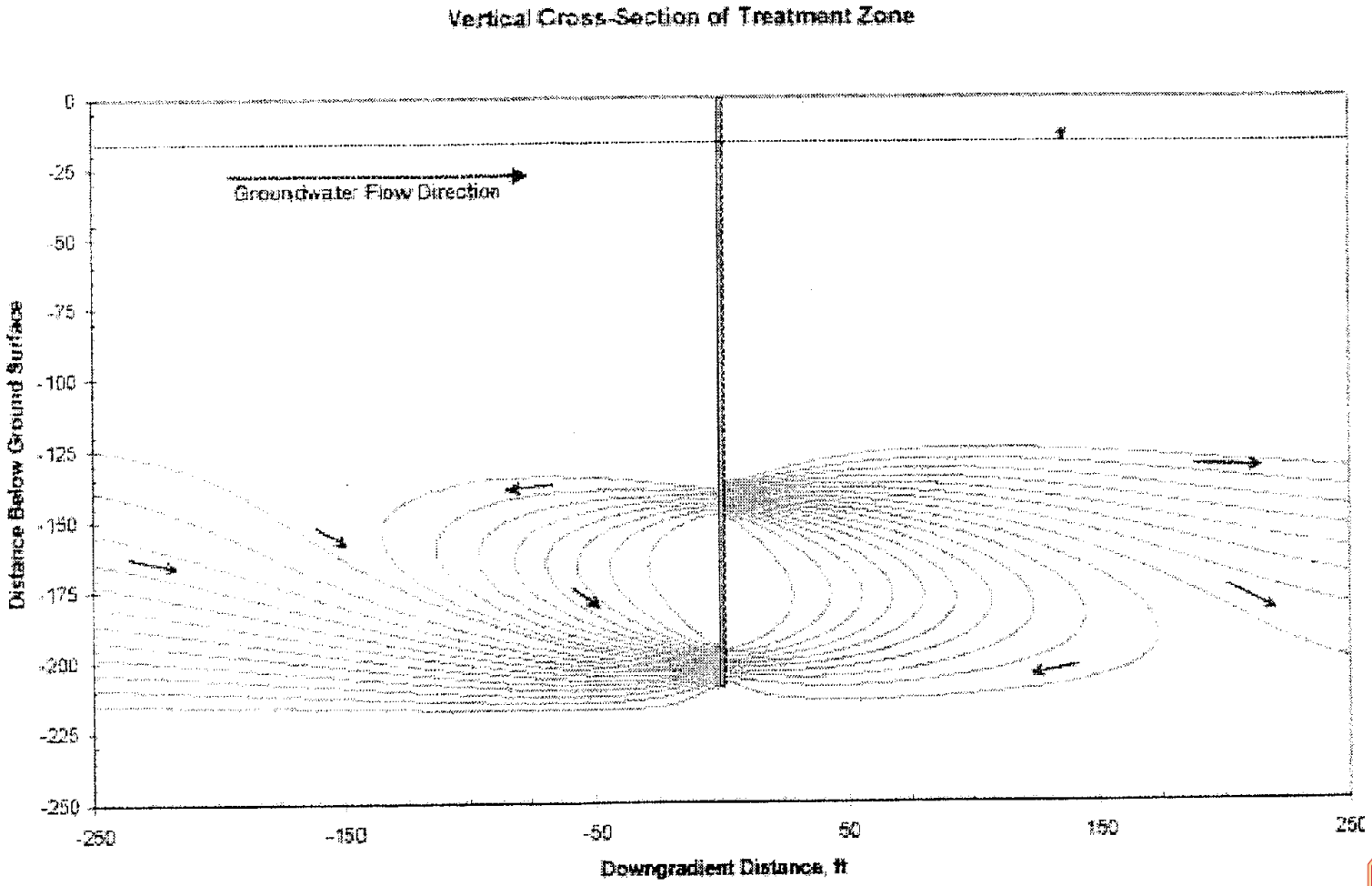
Above Ground Bioreactors

- Contaminant plume captured by pumping, polished with above ground bioreactor water treatment
- Re-injection of treated water in the formation to enhance cleanup
- Able to inject oxygen, acclimated microbes and nutrients into fracture zones to speed up cleanup while you are treating the contaminated groundwater

Recirculating Wells

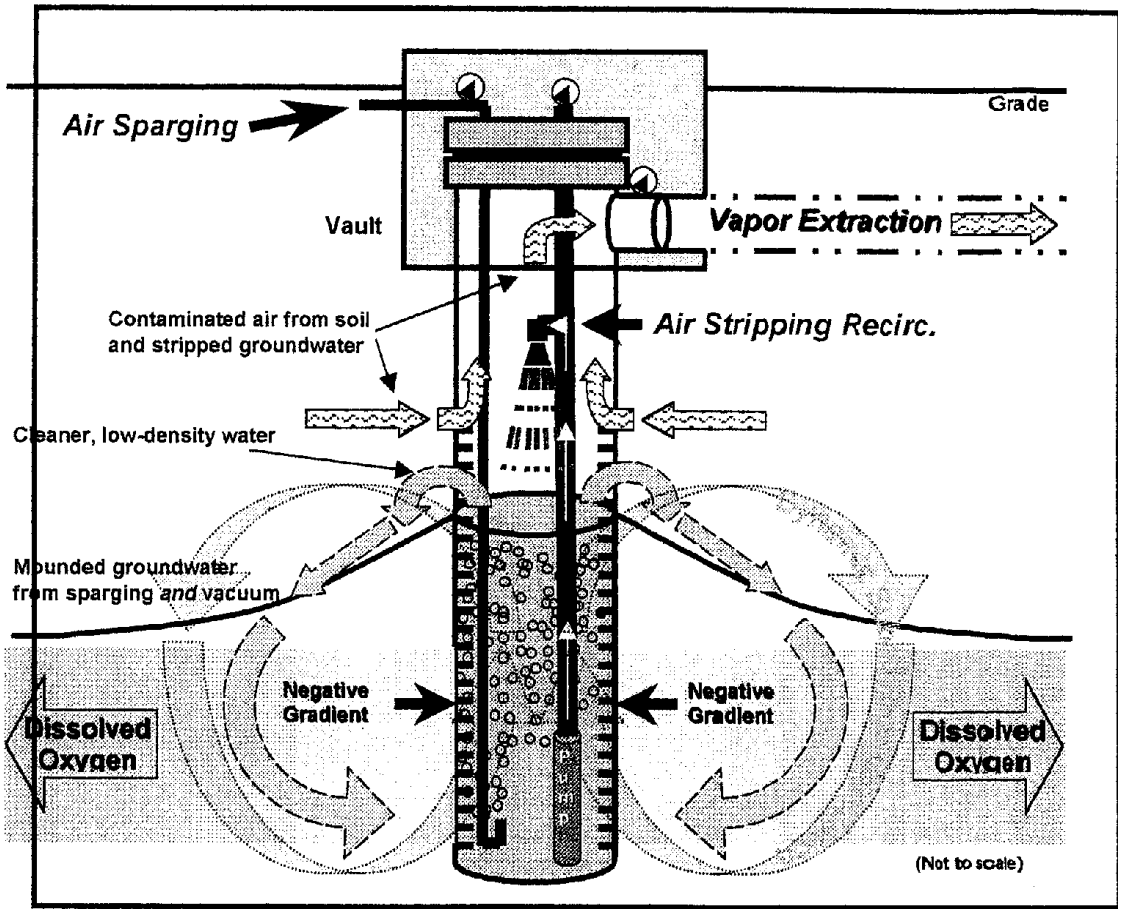
- Uses multiple screens at different intervals and in well treatment to achieve ROI and groundwater treatment, alternative to pump and treat
  - Technology has been around since the 1990s but recent improvements show promise
  - ART™ Wells
  - Geotech Plume Eater™
  - Concerns
    - Biofouling in some groundwater geochemistries
    - ROI uncertain in complex formations

Recirculating Wells (cont.)



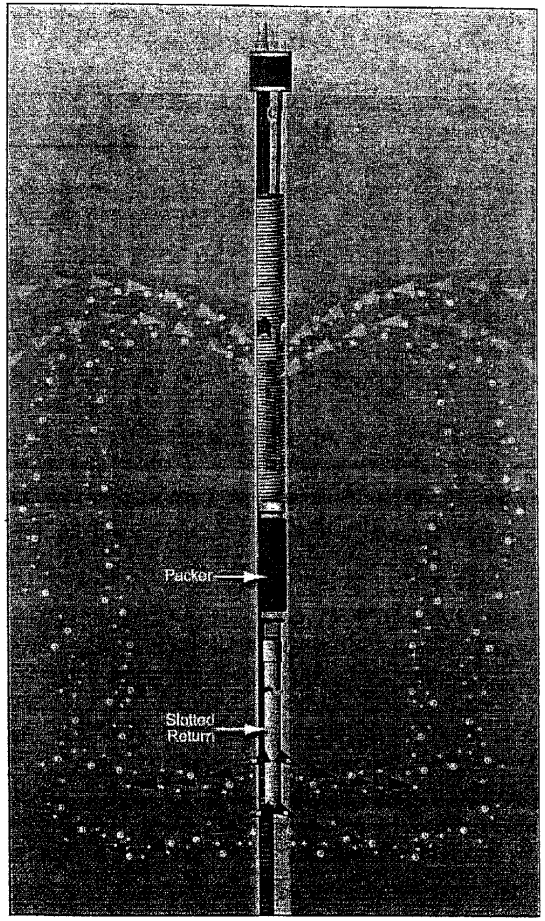
Recirculating Wells (cont.)

- ART™ Wells
  - Adds SVE/Sparge
  - In-well stripping



Recirculating Wells (cont.)

- Geotech Plume Eater™
  - Opposite flow pattern and in well stripping
  - Better ROI

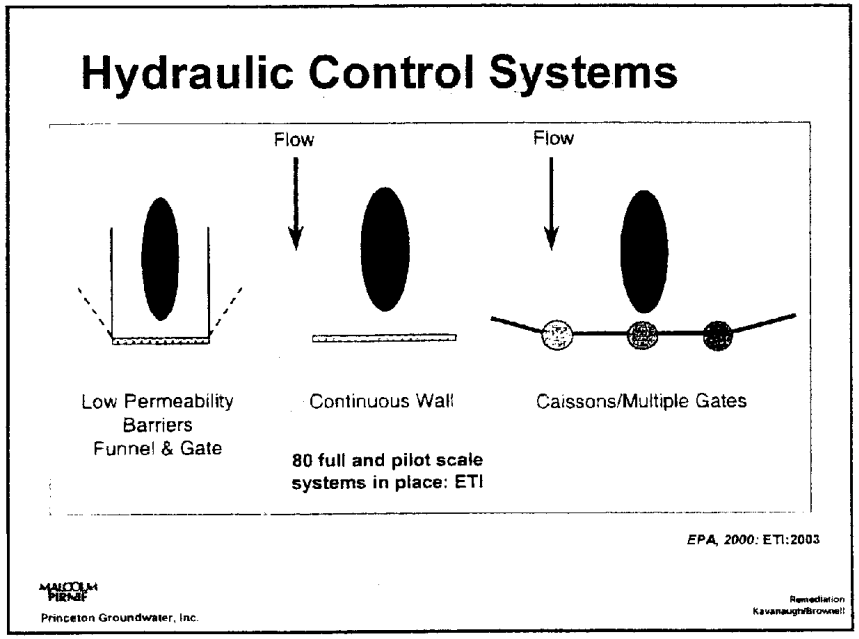


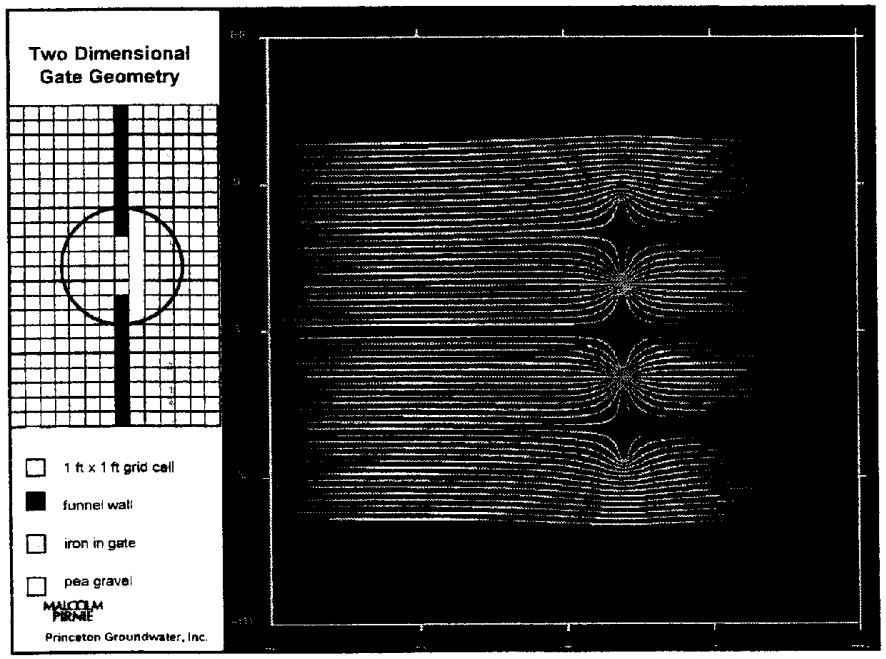
Geotech Plume Eater System

Permeable Reactive Barriers

- Contaminant plume funneled into reactive treatment barrier by impermeable wing walls or hydraulic routing through high permeability walls
- While groundwater moves through reactive treatment barrier it is chemically degraded
- Wing walls prevent down gradient movement of groundwater and direct flow to reactive barrier
- Impermeable wing walls typically constructed of interlocking sheet piling or slurry wall filled with bentonite. Permeable wing walls are typically gravel filled.
- Monitoring wells placed above, inside barrier, and down gradient to monitor performance

Permeable Reactive Barriers (cont.)





Permeable Reactive Barriers (cont.)

- Treatment materials for petroleum
  - ORC, oxidants, diffusers, biobarriers.
- Degrades contaminants, no by-products, no energy source, few above ground structures, low O&M, reactant is inexpensive
- May need to rejuvenate treatment materials (ORC, oxidants)

Permeable Reactive Barrier (cont.)

Concerns

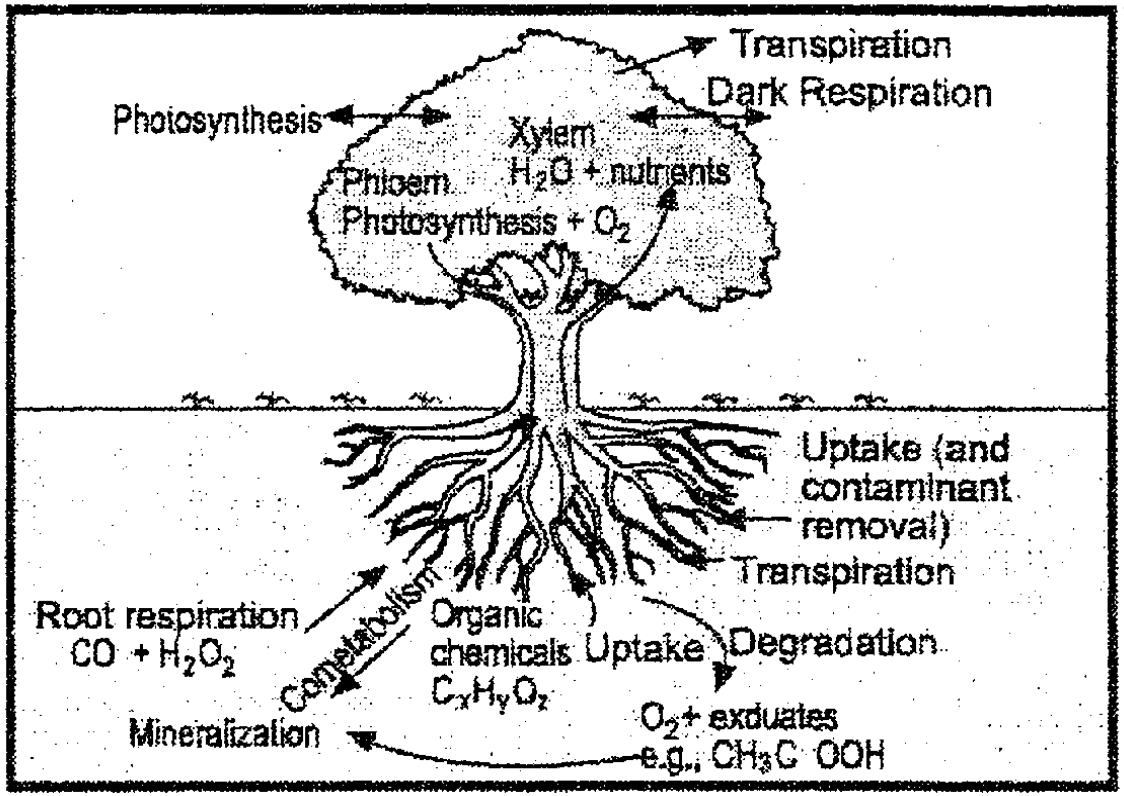
- Can you key into lower confining layer so contaminants don't go underneath?
- Relatively new technology, not much experience in Maryland
- Typically used for larger, well defined plumes
- Requires some construction space
- Initial construction costs may be excessive for small gas station site

Phytoremediation

- Use a barrier of hybrid poplars or other fast growing, deep rooted vegetation to capture down gradient dissolved plume
- In situ, low maintenance, reduced volume for disposal
- Limited to 20 feet depth
- Seasonal variability

Phytoremediation (cont.)

Model of Phytoremediation



EPA, 2002