

Welcome to the Dense Non-Aqueous Phase Liquids (DNAPLs) Site Remediation: Technologies and their Applicability Webinar

Presented by:

Dr Gavin Grant
Geosyntec
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ARCHON
Groundwater & Geoscience

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Presented by:
Jonathan Smith, Shell Global Solutions (UK)
Paul Bardos, i³ environmental technology Ltd

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DNAPL Site Remediation: Technologies and Their Applicability

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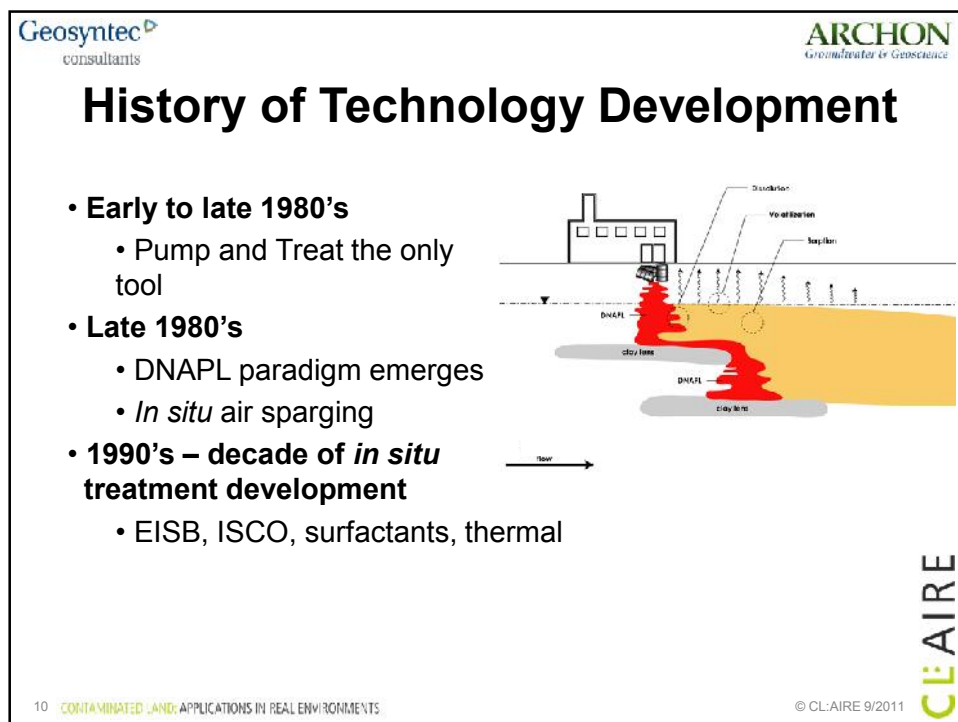
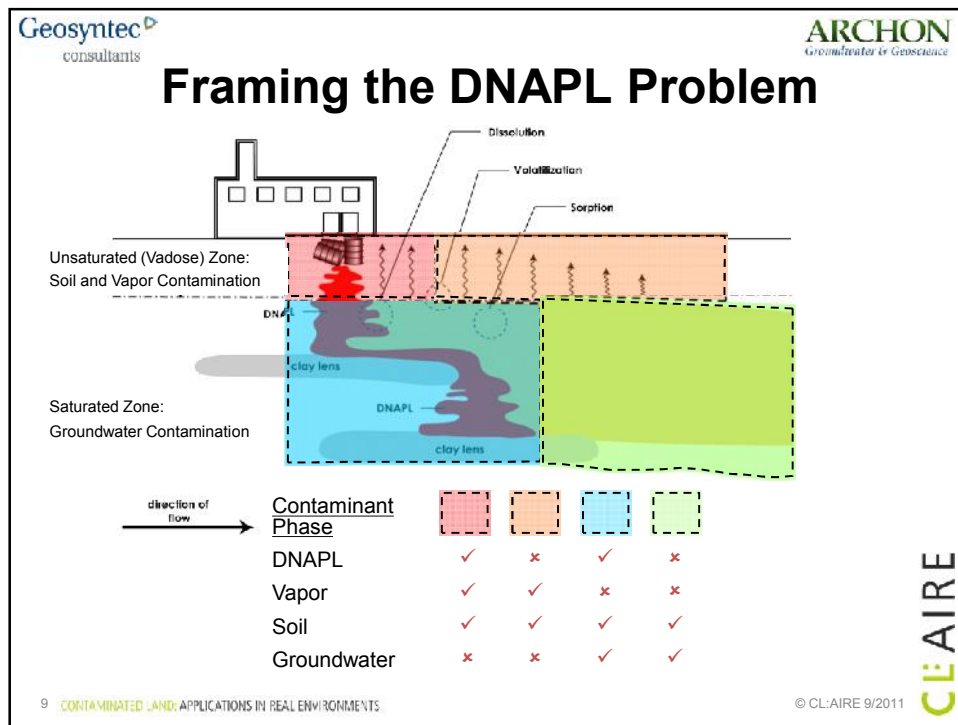


Overview

- **Established DNAPL Remedial Strategies**
 - History of technology development
 - Limitations of *in situ* technologies
- **Recent Advances**
 - BioDNAPL
 - Thermal treatments
 - Combined approaches
- **What is achievable?**

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History of Technology Development

- **2000's**
 - *In situ* application strategies refined
 - Combined remedies / treatment trains emerge
- **2010's**
 - *In situ* technology enhancements (S-ISCO)
 - Novel technologies (e.g., STAR)

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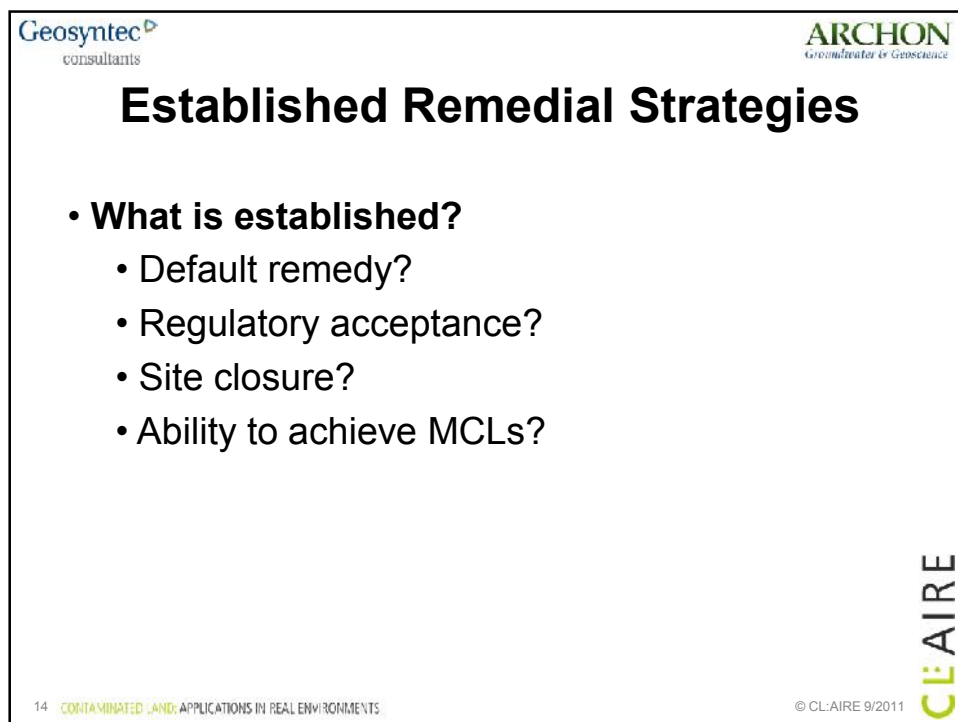
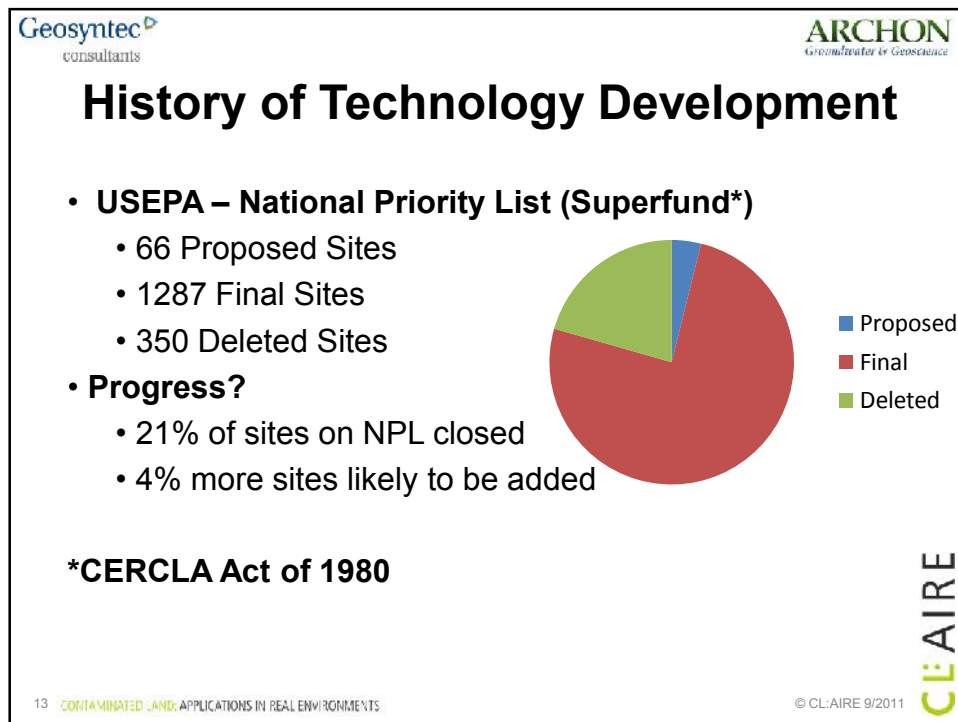


History of Technology Development

- **What have we accomplished?**
 - No “Silver Bullet”
 - Some technologies better suited to certain applications than others
 - Various remedies capable of partial DNAPL mass removal
 - Numerous sites closed
- **MCLs achieved?**
 - Debatable...

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Established DNAPL Technologies and Their Limitations

Technologies that may be considered “established” for remediation of DNAPLs:

- Soil:
 - Dig & Dump
 - Soil Vapour Extraction (SVE)
- Groundwater:
 - Pump & Treat
 - Air Sparging (AS)
- Soil and Groundwater:
 - Vacuum Enhanced Recovery (VER)



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Established DNAPL Technologies and Their Limitations *continued*

Technology	Advantages	Limitations
Soil:		
Dig and Dump (D&D)	Certainty that remedial objectives are achieved. Rapid.	No treatment - transfers contamination. Requires removal of surface plant and other infrastructure. Increasingly costly especially in UK due to escalating Landfill Tax
SVE	<i>In situ</i> removal – less intrusive than D&D.	Requires off gas treatment. Longer treatment compared to D&D. Poor or no treatment in lower permeability zones.
Soil & Groundwater:		
Vacuum Enhanced Recovery (VER)	<i>In situ</i> removal – less intrusive than D&D. Simultaneous soil and groundwater treatment.	No better than P&T in highly permeable aquifers due to excessive groundwater abstraction. Less effective in lower permeability zones.

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Established DNAPL Technologies and Their Limitations <i>continued</i>		
Technology	Advantages	Limitations
Groundwater:		
Pump & Treat	Simple technology, less reliant on specialist suppliers. <i>In situ</i> technology.	Long treatment time and high cost. Likely will not meet treatment goals in sensible timeframe. Biofouling and associated performance loss in abstraction wells.
Air Sparging	Simultaneous stripping and enhanced degradation of contaminants that degrade aerobically. Many DNAPLs readily partition to vapour phase and therefore are treatable by AS.	Requires suitable overlying formation for off gas collection. Requires off gas treatment. Poor treatment in heterogeneous formations due to lower permeability zones and preferential air flow pathways. Causes redox increase that may inhibit anaerobic degradation of chlorinated solvents.

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Limitations of *In Situ* Technologies

- **Why aren't *in situ* remedies more effective?**
 - Backed by good science
 - Easily demonstrated in the lab
 - Long history of knowledge in field of hydrogeology
 - Knowledge bolstered by extensive experience in oil and gas

Real-world
hydro/geo/bio/chemical
processes are complex!

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Limitations of *In Situ* Technologies

- **Geological limitations**
 - DNAPL architecture complex and unknowable
- **Technologies primarily reagent based**
 - Delivery of reagents impossible to predict
- **Competing processes**
 - methanogenesis for EISB
 - Natural Oxidant Demand for ISCO
- **Unintended consequences:**
 - Well fouling
 - Injection fluid short-circuiting
 - Increasing concentrations



Bio-fouling on pump

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Contents

- Established DNAPL Remedial Strategies
 - History of technology development
 - Limitations of in situ technologies
- **Recent Advances**
 - BioDNAPL
 - Thermal treatments
 - Combined approaches
- What is achievable?

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Recent Advances – In Situ Bioremediation

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In Situ Bioremediation (ISB): engineered enhancement of subsurface microbiological activity, generally involving application of carbon substrate to degrade DNAPL contaminants by stimulation of reductive dechlorination.

Reductive pathway for PCE/TCE (reproduced from ITRC, 2008)

Development status of ISB:

- Proven technology for treatment of dissolved phase DNAPL contaminants - PCE, TCE, TCA, cDCE, VC, etc.
- Developing technology for treatment of DNAPL source zones

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In Situ Bioremediation

How ISB Works at DNAPL Source Zones

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- Enhance the dissolution and desorption of contaminant at the water/DNAPL Interface
 - degradation does not occur within the DNAPL phase
- Stimulate microbial degradation of DNAPL to ethene/ethane/other low hazard end products
- Reduce the mass of DNAPL source

After ITRC 2008 "In situ bioremediation of chlorinated ethene - DNAPL source zones"

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***In Situ* Bioremediation Overview of Application at DNAPL Source Zones**

- **Deliver carbon donor, together with nutrients, alkaline buffer and/or bacterial culture to the treatment zone(s) to:**
 - Modify/Control aquifer redox and pH
 - Initiate/Enhance dechlorination
 - Dissolve/desorb and degrade DNAPL mass
- **Operate and Monitor:**
 - Monitor process parameters – pH, redox, TOC, etc }
 - Monitor performance – target contaminant concentrations }
 - Adjust conditions – TOC, redox, pH, microbiology - to maintain optimum performance and ensure complete dechlorination

ISB is a dynamic biochemical process – regular monitoring and system adjustment required

- **Verify:**
 - Attainment of treatment goal

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***In Situ* Bioremediation Overview of Application at DNAPL Source Zones**

- **Design Considerations:**
 - Electron donor selection
 - Soluble donors – molasses, lactate, methanol, ethanol
 - Slow-release donors – EVO, chitin, whey, polymers
 - Partitioning donors – EVO, alcohols
 - Electron donor dosing – stoichiometric calculation
 - Electron donor delivery method and effectiveness
 - Biostimulation; or Biostimulation + Bioaugmentation
- **O&M Considerations:**
 - Frequency of electron donor re-application
 - Biofouling
 - Post-treatment monitoring period – possible rebound timescales

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In Situ Bioremediation – Key Challenges

Challenge	ISB	P&T	ISCO
Low permeability/Heterogeneity/Preferential pathways (and consequent rebound due to incomplete treatment)	●	●	●
Long treatment times	●	●	○
Biofouling	●	●	
Other Operation and Maintenance	○	●	●
Potential for mobilisation of contaminants	○	○	●
Unfavourable geochemical conditions	●	●	●
Absence of appropriate bacteria	●		
Potential for mobilisation of metals	●	○	●
Inhibition/toxicity of contaminants / co-contaminants	●		

Many of these challenges are not unique to ISB and can be solved by appropriate engineering.

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In Situ Bioremediation Case Study – SABRE Research Site

SABRE: 5 year collaborative project carried out by a team from UK, US and Canada:

- Field demonstration over ± 600 days in a densely-instrumented contained test cell with separate larger uncontaminated area.
- Extensive site characterisation prior to cell construction.
- Supported by:
 - laboratory microcosm and column testing.
 - Process modelling studies

In Situ Source Area BioREmediation

To evaluate the performance of enhanced anaerobic bioremediation for the treatment of DNAPL source areas

<http://www.claire.co.uk/sabre.php>

Logos: LINK, dti (Department of Trade and Industry), EPSRC, sobre, Streamtube, Geosyntec consultants, ENVIRONMENT AGENCY, NATURAL ENVIRONMENT RESEARCH COUNCIL.

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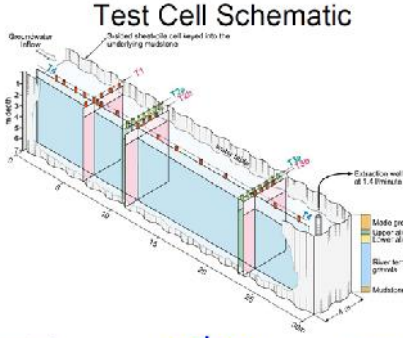
In Situ Bioremediation Case Study – SABRE Research Site

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- Selected electron donor: emulsified vegetable oil (EVO)
- Test cell was Bioaugmented with KB-1 culture.
- Operational issues:
 - pH reduced to below optimum (<6.5) - controlled by Bicarbonate amendment
 - Aquifer fouling resulted in difficulty in maintaining constant groundwater flux into and through cell.



Test Cell Schematic



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In Situ Bioremediation Case Study – SABRE Research Site

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- **Principal Findings:**
 - Substantial transformation of TCE to cDCE, and partial dechlorination of cDCE to VC and ethene.
 - Chlorinated ethene flux enhancement factor: ± 1.6
 - Total mass removed: 900 kg as TCE (of the order of 50% source mass reduction).
 - Substantial dechlorination in presence of high sulphate.
 - Significant VC and ethene produced but cDCE remained dominant CE at end of test period.
 - pH control needed.

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In Situ Bioremediation Technology Capabilities and Relative Costs

- **Summary of ISB Capabilities:**
 - Demonstrated mass removal in DNAPL source zones (SABRE, other projects in USA & Canada)
 - Treatment timescales measured in years
 - Costs likely low/lowest relative to alternatives
 - Cost certainty similar to alternate in situ technologies, but inferior to ex situ alternatives

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In Situ Bioremediation Technology Capabilities and Relative Costs

- **Costs Comparison:**
 - Cost estimates for full scale treatment of the SABRE Research Site¹
 - Cost model results reported by ESTCP/Geosyntec² for hypothetical site

Parameter	SABRE ¹	ESTCP/Geosyntec ²
Site	SABRE – UK, Midlands	Hypothetical, modelled
Source mass assessed (TCE, tonnes)	20	5.6
Aquifer Type	Unconsolidated alluvial	
Total Treatment Costs:		
ISB	£1.5M	£1.1M
Chemox	£3.0M	£1.75M
Other Technologies	Thermal: £2.5M	P&T: £2.0M

¹ CL:AIRE report "Overview of the SABRE Field Tests", CL:AIRE Report SAB 5, September 2010
² ESTCP "Remediation of DNAPL through Sequential In Situ Chemical Oxidation and Bioaugmentation", ESTCP Project ER-0116, April 2009

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Thermal Technologies

- **Thermal Remediation Overview**
- **Types of Thermal Remediation:**
 - Steam Enhanced Extraction (SEE)
 - Electrical Resistive Heating (ERH)
 - *In Situ* Thermal Desorption (ISTD)
 - Self-Sustaining Treatment for Active Remediation (STAR)
- **Head-to-Head Comparison**
- **Case Studies**

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Thermal Remediation Overview

- Heat applied to facilitate contaminant mobilization, solubilization, removal, destruction and/or degradation
- Thermal Techniques include:
 - SEE
 - ERH
 - ISTD
 - STAR
- Typically applied in NAPL source Areas
- Implemented in conjunction with Soil Vapor Extraction (SVE) systems to contain and recover vapors

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Steam Enhanced Extraction

The diagram illustrates the SVE process. A contaminated spill is heated by steam, causing contaminants to volatilize. The steam/hot water flow is shown moving from the injection well into the ground. An extraction well with a submersible pump draws the contaminated water, which then passes through a series of separators (Vapor/Liquid, Oil/Water, Water) and is eventually recycled. Off-gases are captured by a vacuum pump and treated.

Steam injected into source zone to dissolve, vaporize and mobilize contaminants that are recovered using SVE

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Electrical Resistive Heating (ERH)

- Application of electrical current through subsurface generates heat
- Steam generation dissolves, vaporizes and mobilizes contaminants which are recovered using SVE

Fort Lewis, Washington

The diagram shows the ERH system components: a 13.8 kV local service, a voltage control system, a network of electrodes forming an electrically heated region, a contaminated zone, and a vacuum system that removes vapor and directs it to a screened venting well.

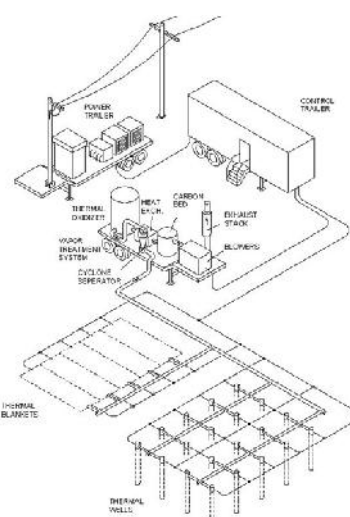
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In Situ Thermal Desorption (ISTD)



- Application of heat using:
 - array of vertical heater elements and vacuum wells; or
 - a surface blanket of heaters and vacuum shroud at surface (less common)
- ISTD can achieve high temperatures (>500 °C) - causes contaminant oxidation and pyrolysis



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Self-Sustaining Treatment for Active Remediation (STAR)

- Smoldering combustion reaction deriving energy from contaminants
- High temperatures (>1000 °C) destroys contaminants in place




Before After

Pitt Consol, Newark, New Jersey

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Head-to-Head Comparison

	<u>ERH</u>	<u>ISTD</u>	<u>STAR</u>
Temperature	< 100 °C	< 500 to 700 °C	>1000 °C
Mechanisms	Volatilization, steam stripping	Oxidation, pyrolysis	Smoldering combustion
Energy Requirements	Continuous	Continuous	Localized short duration
Operational Timeframe	Weeks to Months	Months	Days to Weeks
Cost	\$100 to \$140/CY	\$150 to \$300/CY	\$60 to 120/CY

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Head-to-Head Comparison - ERH

<u>Benefits</u>	<u>Limitations</u>
Rapid source area treatment	Energy intensive
Unaffected by Heterogeneity	Potential high costs
Conducive to bioremediation polishing	Not suitable for all compounds of interest
	Requires collection and treatment of vapors

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Head-to-Head Comparison - ISTD

Benefits	Limitations
Rapid source area treatment	Energy intensive
Unaffected by Heterogeneity	Potential high costs
In situ contaminant destruction (oxidation/pyrolysis)	Possibly produce toxic byproducts

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Head-to-Head Comparison - STAR

Benefits	Limitations
Rapid source area treatment	Collection of vapors may be required
Low energy requirements	Generally used for low-volatility DNAPLs
In situ contaminant destruction	Minimum concentrations / saturation to be self-sustaining
Targeted and controllable	

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STAR Case Study (NJ)

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- Former Cresol Manufacturing Facility in Newark, New Jersey
- 37 acre site – currently shipping container storage yard
- Proposed remedy was excavation and disposal of >300,000 CY of soil
- STAR Evaluation:
 - Treatability study
 - *In Situ* pilot test



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Objectives

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- Test designed to evaluate STAR:
 - At a large scale
 - Under saturated conditions (i.e., below ground surface and below the water table)
- Quantify mass destruction rates and remediation efficiency
- PTA – 20 by 60 feet, 10-foot thick fill unit



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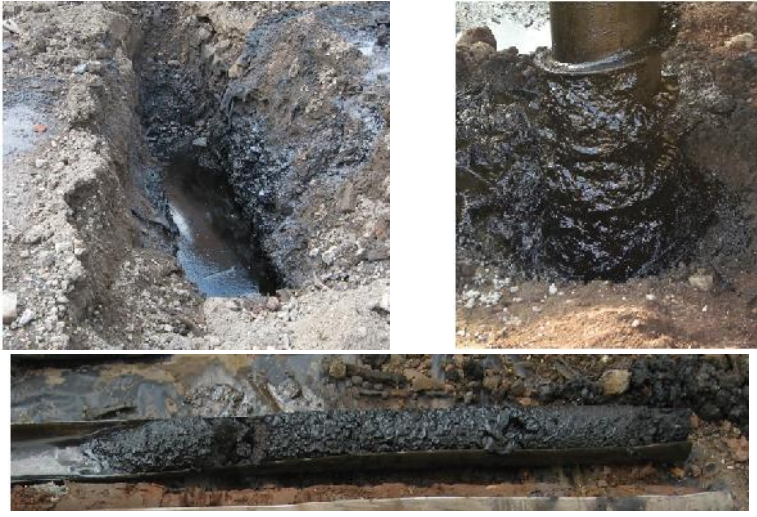
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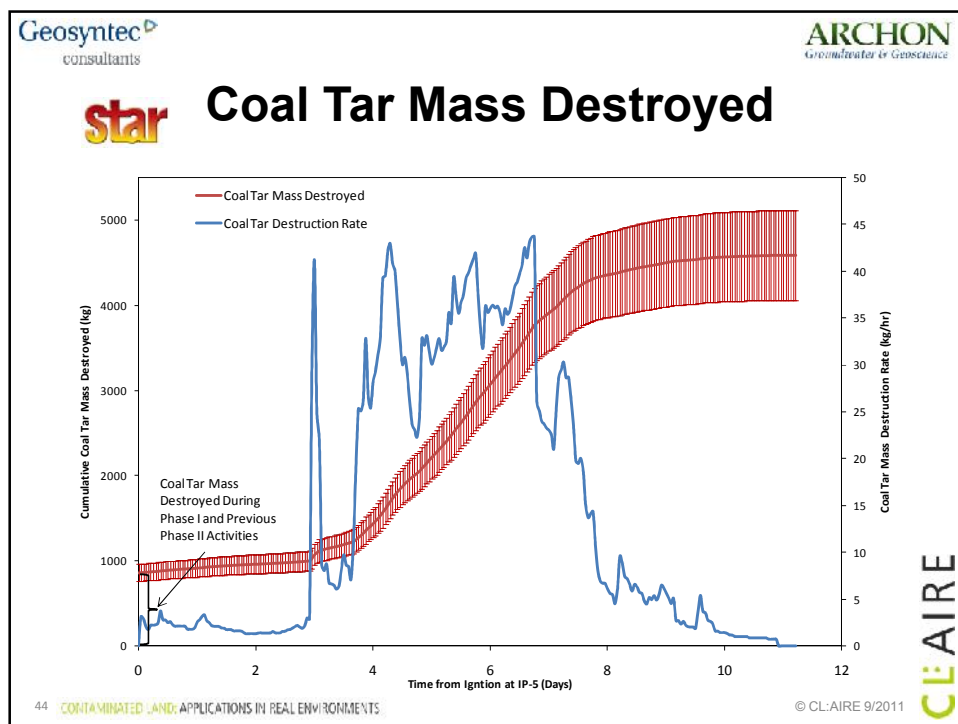
star Pre-pilot Characterization



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Post-Pilot Results

Before



After



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Post-Pilot Results

Before



After



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Post-pilot Soil Sampling

Compound	Average Concentration (mg/kg)	
	Before STAR Treatment	Combustion Zone T > 600 °C
2,4-Dimethylphenol	635	1
2-Methylnaphthalene	7,900	10
2-Methylphenol	475	3
4-Methylphenol	595	5
Acenaphthene	3,950	6
Acenaphthylene	295	1
Anthracene	16,700	10
Benzene	36	0
Benzo(a)anthracene	775	2
Benzo(a)pyrene	505	1
Benzo(b)fluoranthene	640	2
Benzo(g,h,i)perylene	255	1
Benzo(k)fluoranthene	240	1
Carbazole	6,750	2
Chrysene	870	3
Dibenzo(a,h)anthracene	60	0
Dibenzofuran	3,850	7
Ethylbenzene	40	0
Fluoranthene	3,750	11
Fluorene	5,150	7
Indeno(1,2,3-cd)pyrene	220	1
Naphthalene	29,500	63
Phenanthrene	10,850	21
Pyrene	2,550	8
Toluene	130	0
Xylenes (total)	225	0
TPH-DRO soil C10-C28*	118,000	243
TPH-GRO soil C6-C10	1,300	7

Average
Concentration
Reduction = **99.72%**

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Geosyntec consultants star		ARCHON Groundwater & Geoscience		Pilot Test Summary	
• Almost 5 tons of coal tar destroyed (below ground surface and below the water table) • Concentration reductions of 3-4 orders of magnitude • Post-pilot concentrations below NJDEP criteria • Combustion front propagation up to 30 feet observed • Sustained destruction rates as high as 800 kg/day at a single well • Continued STAR development planned for Site – complete full-scale implementation by December 2015					
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Combined Remedies

- **What are combined remedies?**
- **Types of combined remedies**
 - Sequential
 - Concurrent
 - Coupled process combinations
 - Contingent or conditional combinations
- **Application of combined remedies**
- **Case study**

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Combined Remedies

- **Definition:**
 - Any remediation that uses more than one technology
- **Purpose:**
 - Improved performance when single technology can not achieve adequate remediation
 - Harness synergistic interactions between different phys/chem/bio process
 - Improved resource efficiency (i.e., right time and place)

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Combined Remedies

- **Types:**
 - **Sequential** (off set in time and independent)
 - e.g., Thermal followed by MNA
 - **Concurrent** (applied at same time in different areas)
 - e.g., ISCO in source, biobarrier at perimeter
 - **Coupled** (more than one phys/chem/bio process applied together)
 - e.g., S-ISCO
 - **Contingent or Conditional**

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Combined Remedies

- **Keys to successful application:**
 - Implementation **approach**
 - understand capabilities of single technologies
 - Understanding of **residual effects** of previous technologies
 - take advantage of synergies / be aware of complicating factors)
 - Clear **transition plan**
 - performance metrics for each phase)

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Geosyntec consultants

ARCHON
Groundwater & Geoscience

Sequenced Technologies: Bioremediation Following Thermal Treatment



Courtesy of: Evan Cox, Leah MacKinnon, and Cory Repta (Geosyntec)

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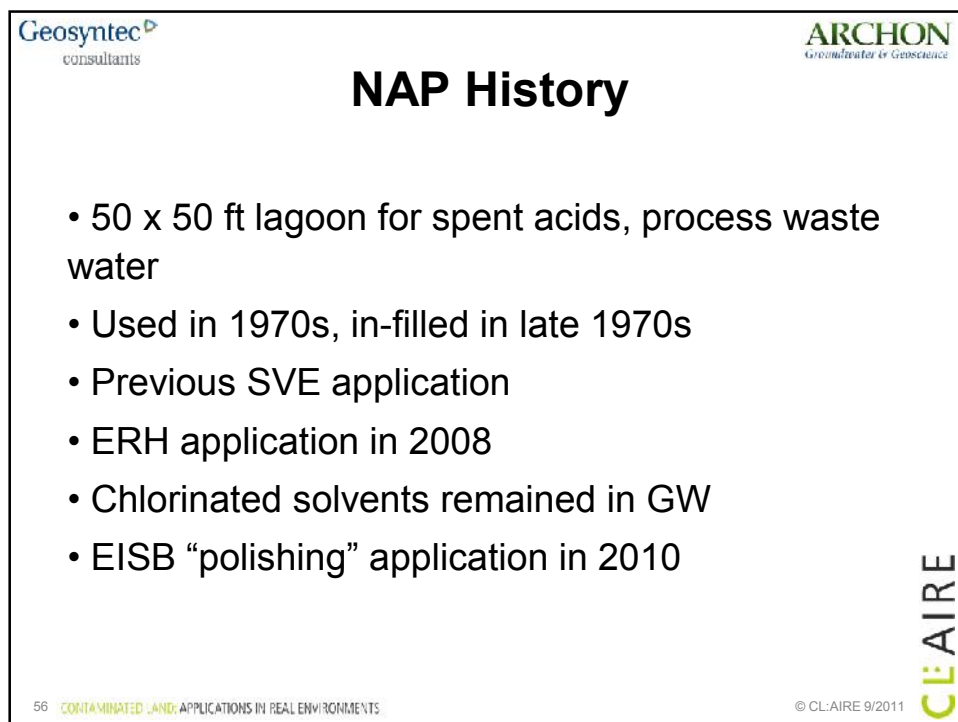
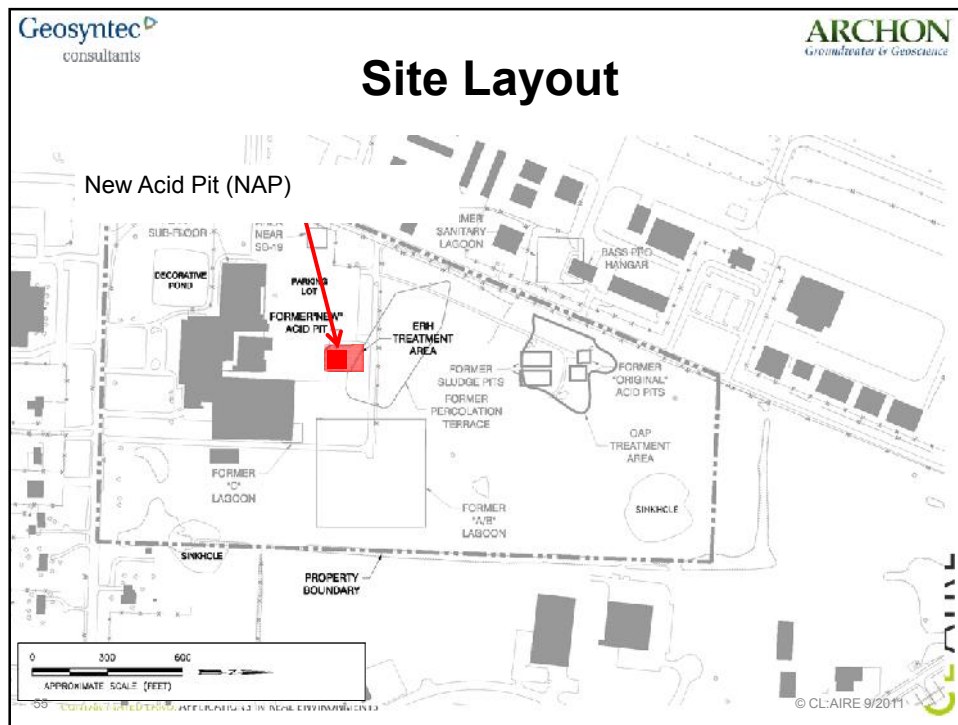
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Basis for Thermal-Bio: Key Findings

1. Soil heating releases organic carbon - potential electron donor ☒
2. Soil heating reduces microbial community composition (methanogens) & dechlorination capability ☐
3. Optimal dechlorination rate for *Dehalococcoides* occurs at 30 to 35°C ☒
4. Bioaugmentation quickly re-establishes microbial community – highly efficient (no competition) ☒

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Geosyntec consultants

ARCHON
Groundwater & Geoscience

ERH Layout & Infrastructure



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ERH Application

- Surface cap of asphalt / concrete
- Potassium citrate electrolyte
- >80 electrode wells installed
- Heating started June 2008
- Soil sampling confirmed remedial objective met (TCE <400 µg/kg)
- ERH shut down January 2009

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Post-ERH Bioremediation Application

Objectives

- Inject slow-release electron donor
 - Emulsified Vegetable Oil (EVO)
- Take advantage of residual ERH heat to promote rapid VOC dechlorination
- Flexible design to accommodate uncertainties

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Implementation: Bedrock



Bedrock Recirculation Setup:
RW-9 (IW)

NAP-RW-101 (EW)

Tanks for GW injection
& recirculation

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Implementation: KB-1 Plus®



- Bioaugmentation with KB-1 Plus®
- Promotes complete dechlorination of both TCE and TCA
- Added 'midstream' to push out from injection wells
- 1-2 L per ERH well

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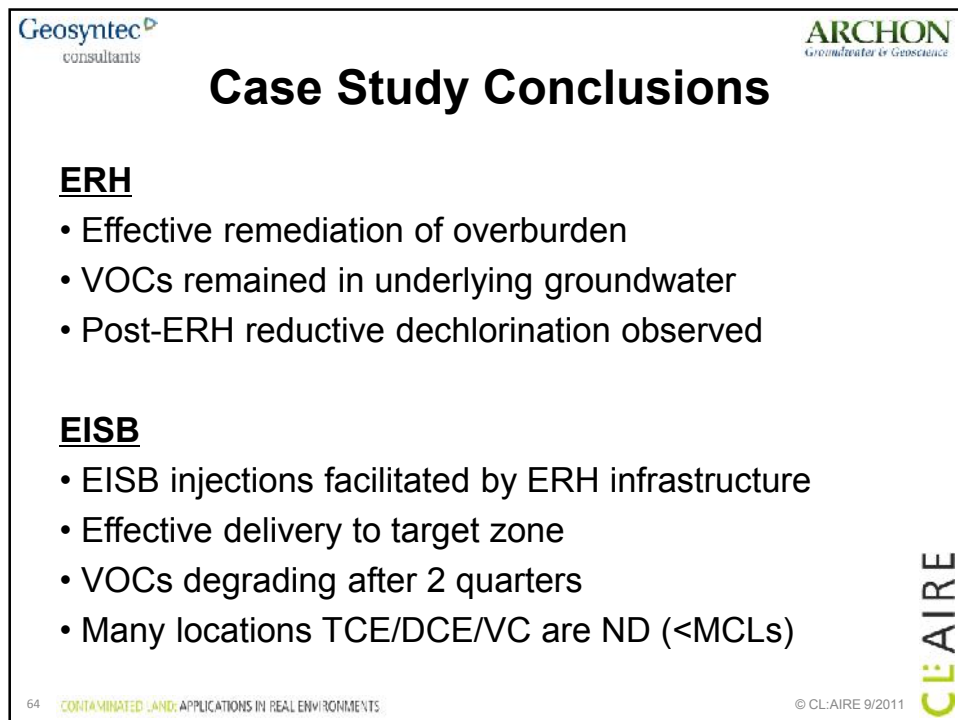
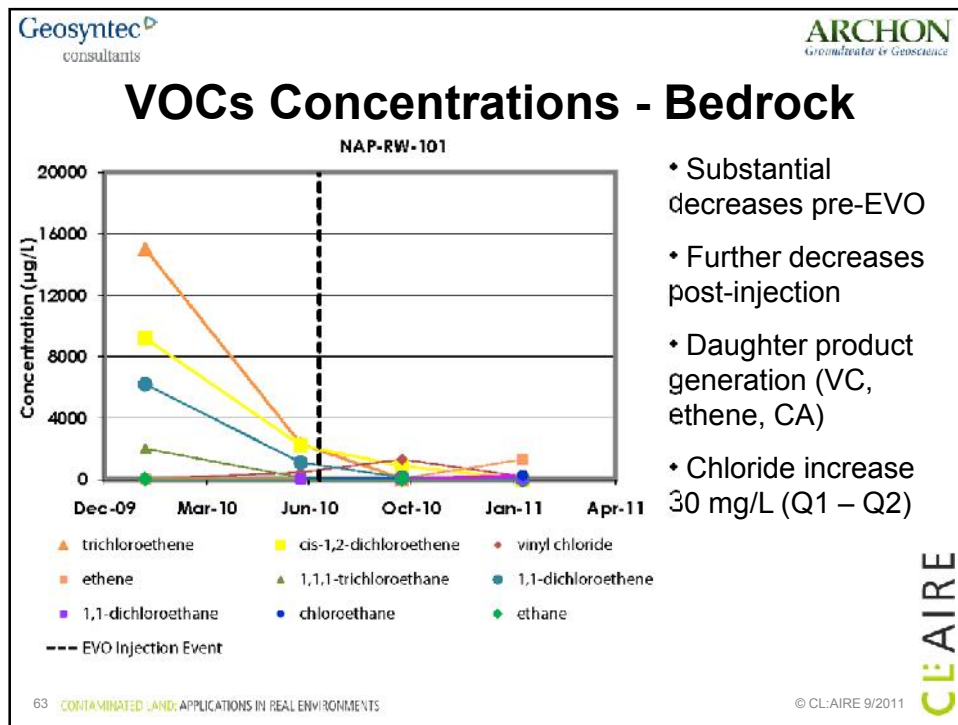
EISB Performance

Parameter	General Result
Methane	>10,000 µg/L
DO, ORP	DO < 1mg/L, ORP < -70 mV
Anions – SO ₄ , NO ₃ Cl	Nitrate and sulfate near depleted Chloride increase by 10 to 100 mg/L from Q1 to Q2
TOC	Increase by >100 mg/L
<i>Dehalococcoides</i>	Increase by Order of Magnitude
pH	Temporary decrease
ERH Residual Heat	Post-ERH (Jan '10): up to 37°C Baseline (June '10): 26 - 37°C Q1 (Sept '10): 28 - 34°C Q2 (Jan '11): 17 - 26°C

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Contents

- Established DNAPL Remedial Strategies
 - History of technology development
 - Limitations of *in situ* technologies
- **Recent Advances**
 - BioDNAPL
 - Thermal treatments
 - Combined approaches
- What is achievable?

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What is Achievable?

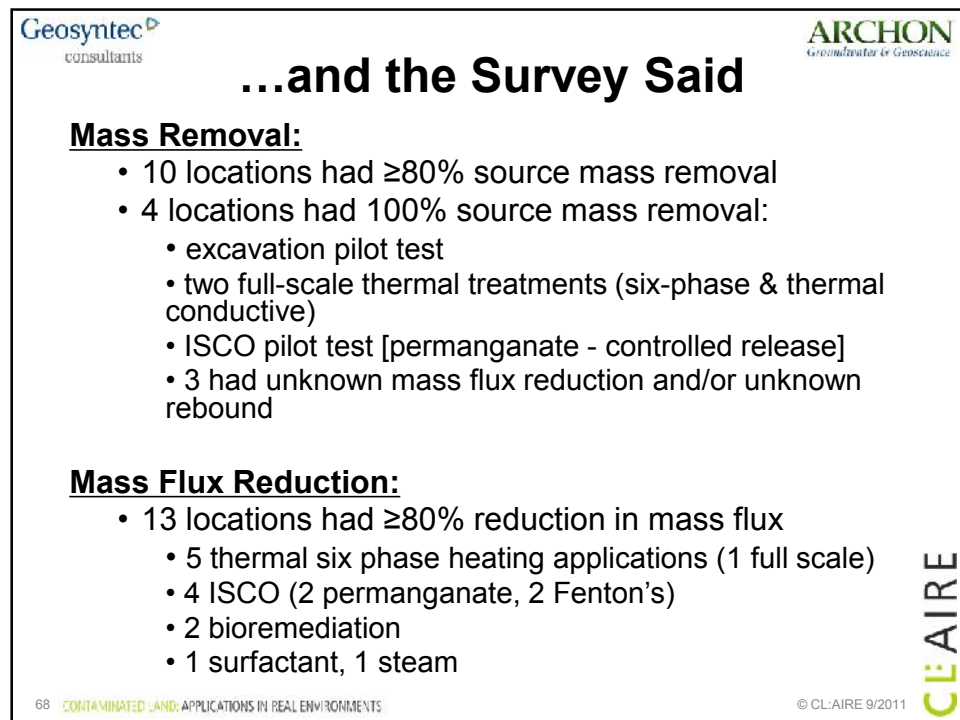
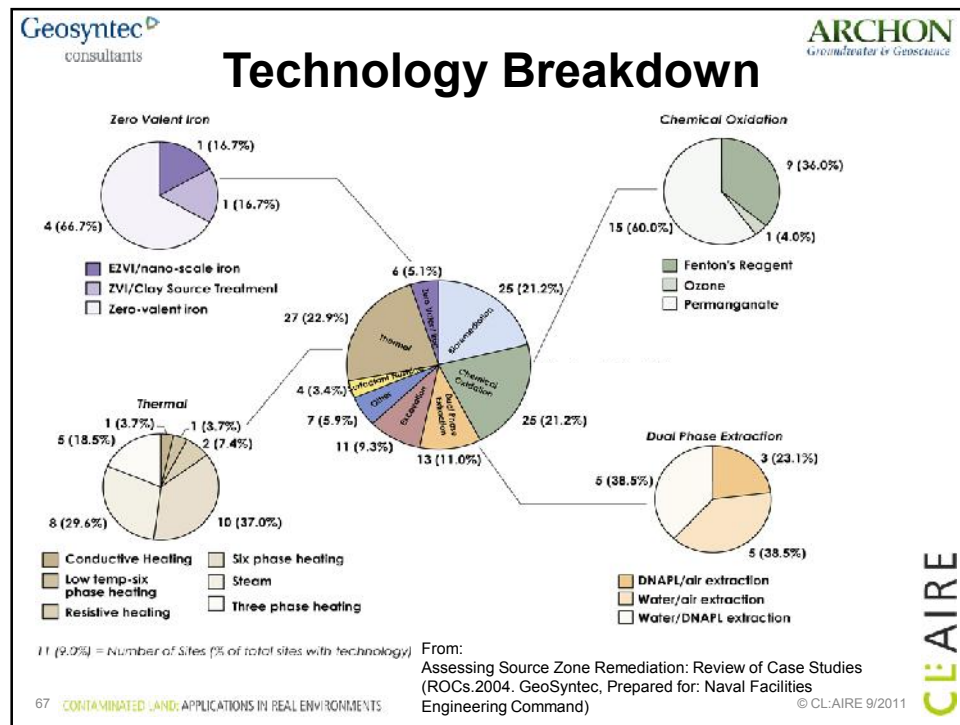
Review of Source Remediation Case Studies:

- Geosyntec survey for U.S. Navy in 2004
- Data obtained from 139 locations
- Source remediation success evaluated by:
 - Estimate of mass removal
 - Decrease in mass flux
 - Occurrence of rebound
 - MCL or site closure

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DNAPL Remediation Technology Screening Tool

- Environmental Security Technology Certification Program (ESTCP)
- Lead by:
 - Naval Facilities Engineering Service Center (NFESC)
 - Geosyntec
 - Queen's University (Bernie Kueper)
 - University of Edinburgh (Jason Gerhard)
- Purpose:

“illustrate which technologies generally work best under specific site conditions and desired remedial outcomes/goals”

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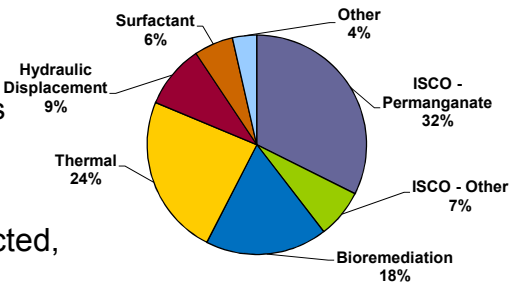
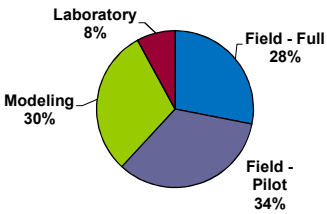
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Case Study Collection

- Case studies entered into database to date:
 - 42 modeling case studies
 - 11 lab studies
 - 86 field case studies
- 20 field case studies collected, still to be entered
- An additional 56 potential case studies identified from other ESTCP project sources
- 70 modeling case studies still in production

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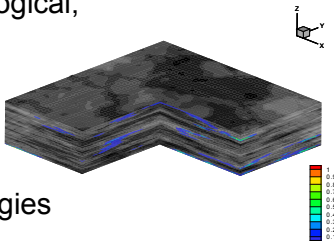
Modeling Approach

Step 1. Create template sites

- Simulate a range of geological, hydrogeological, and chemical environments
- Simulate a range of DNAPL releases and architectures

Step 2. Model DNAPL Treatment

- Simulate treatment with selected technologies
- Metrics evaluated include DNAPL mass reduction, source zone concentration reduction, mass flux reduction, plume length



Template Site

+

Remediation Technology

=

Case study in Screening Tool

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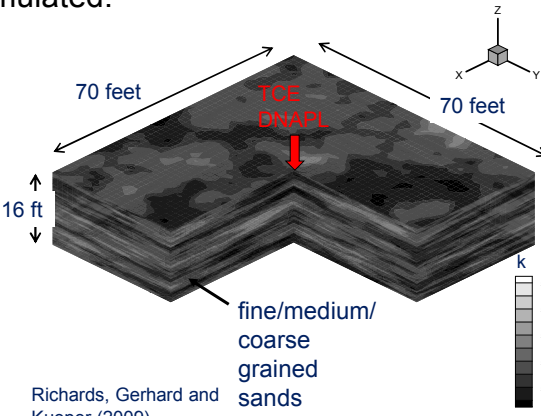
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Modeling Approach

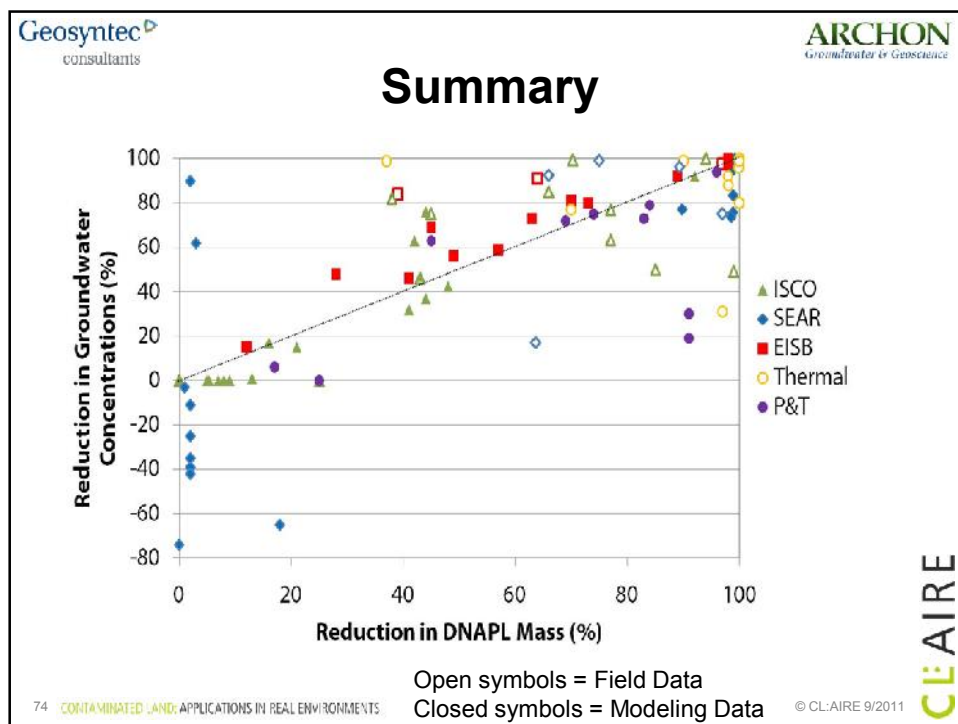
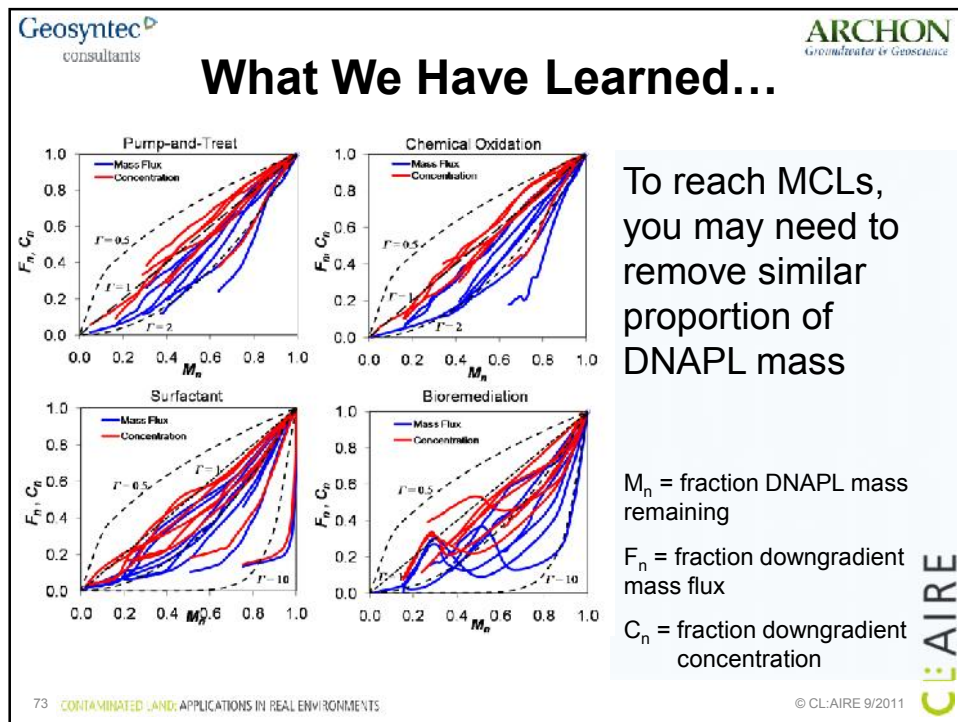
- Field-scale simulations
- Technologies simulated:
 - EISB
 - ISCO
 - HD
 - P&T
 - SEAR

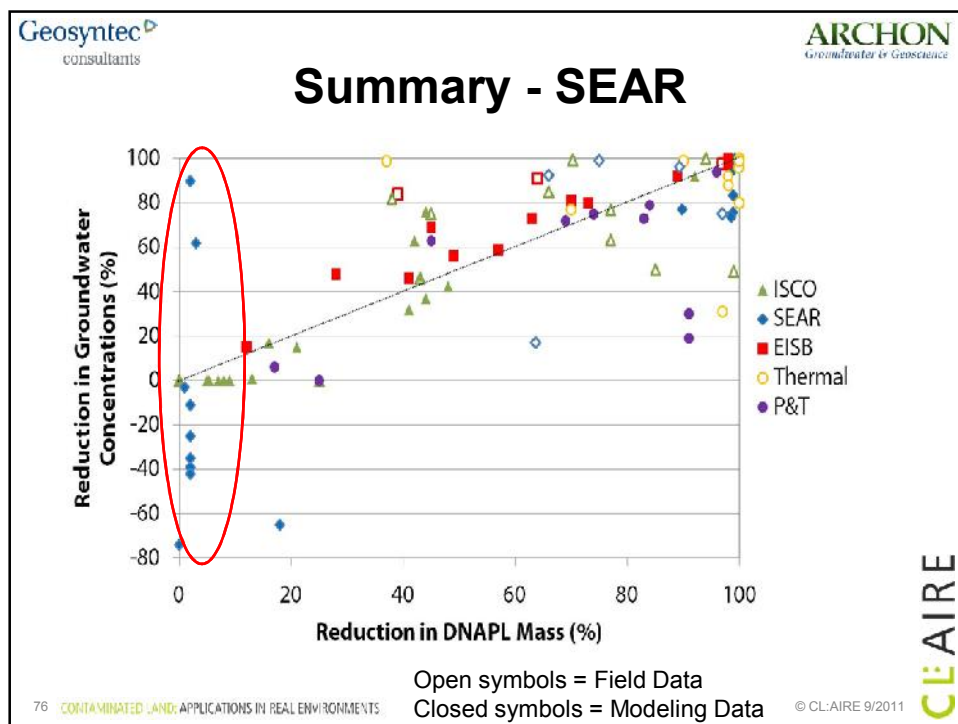
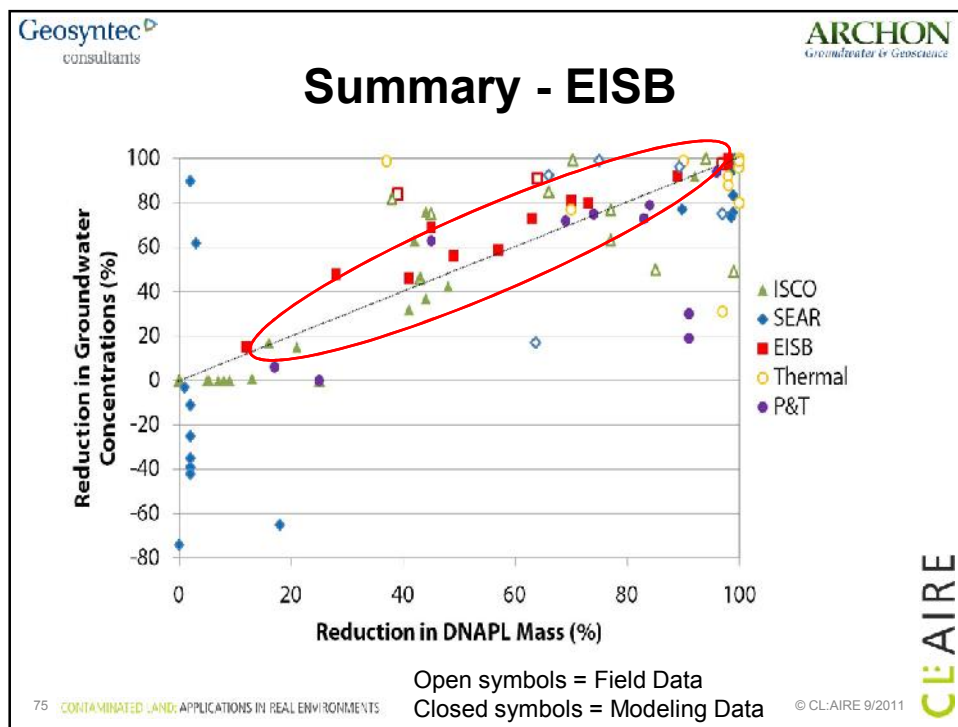


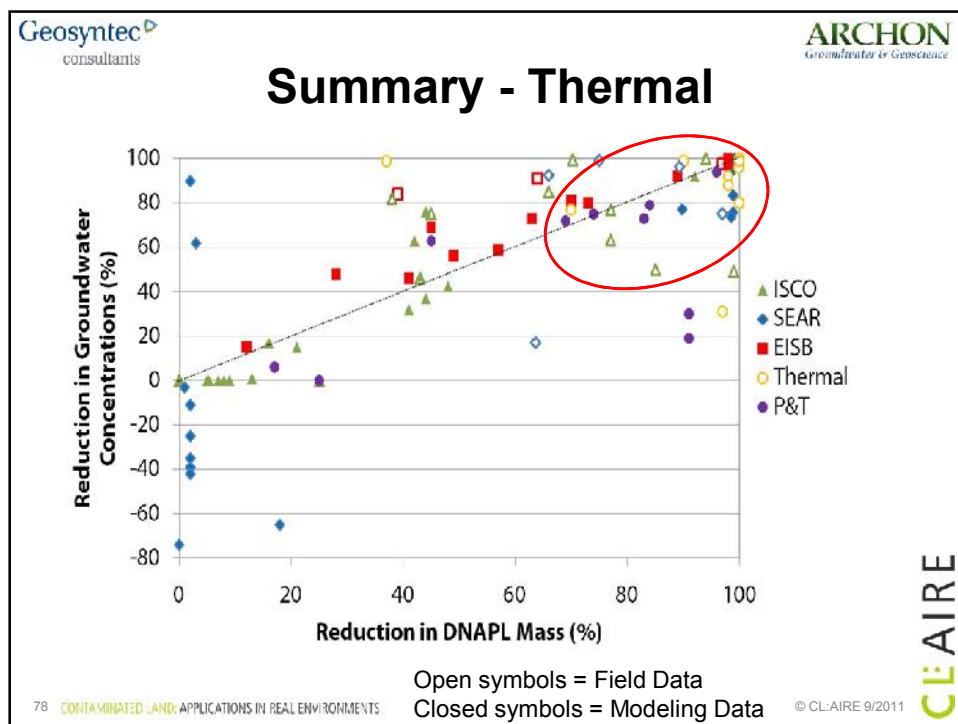
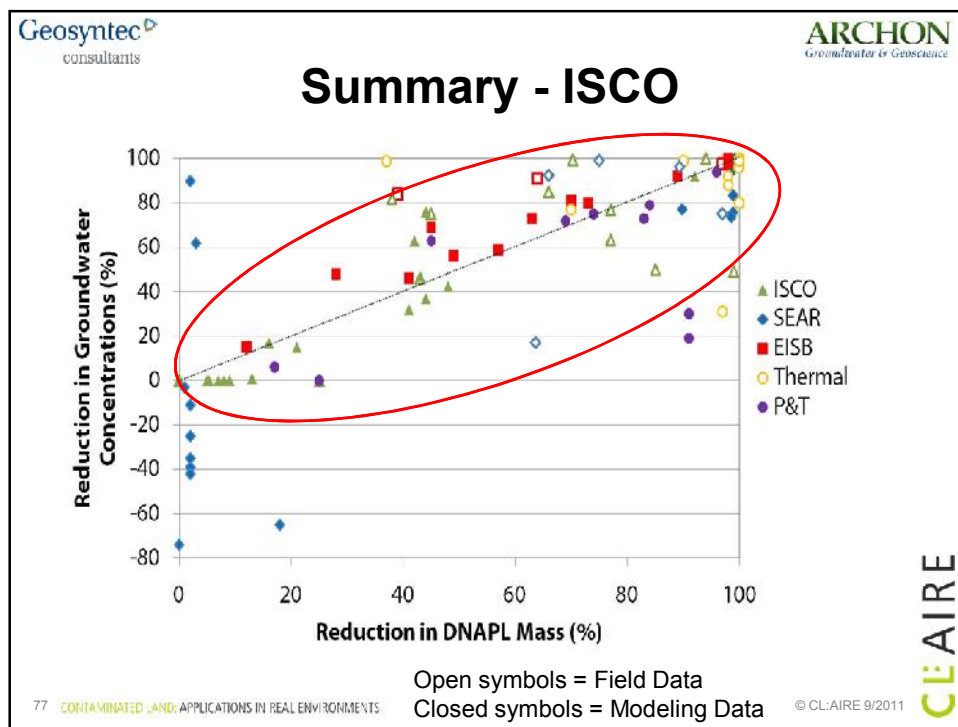
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Conclusions

- **DNAPL Remediation is a complex problem**
- **Lots of tools available**
 - New techniques offer promise
- **Keys to success:**
 - Development of strategy
 - Understanding technologies, their limitations, and synergies with other technologies
 - Managing expectations

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Questions?

Please answer the five multiple-choice questions which will appear on your screen shortly so that we can gain your feedback on today's webinar.

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