In Situ Geochemical Stabilization (ISGS) for NAPL Management

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Presentation Overview

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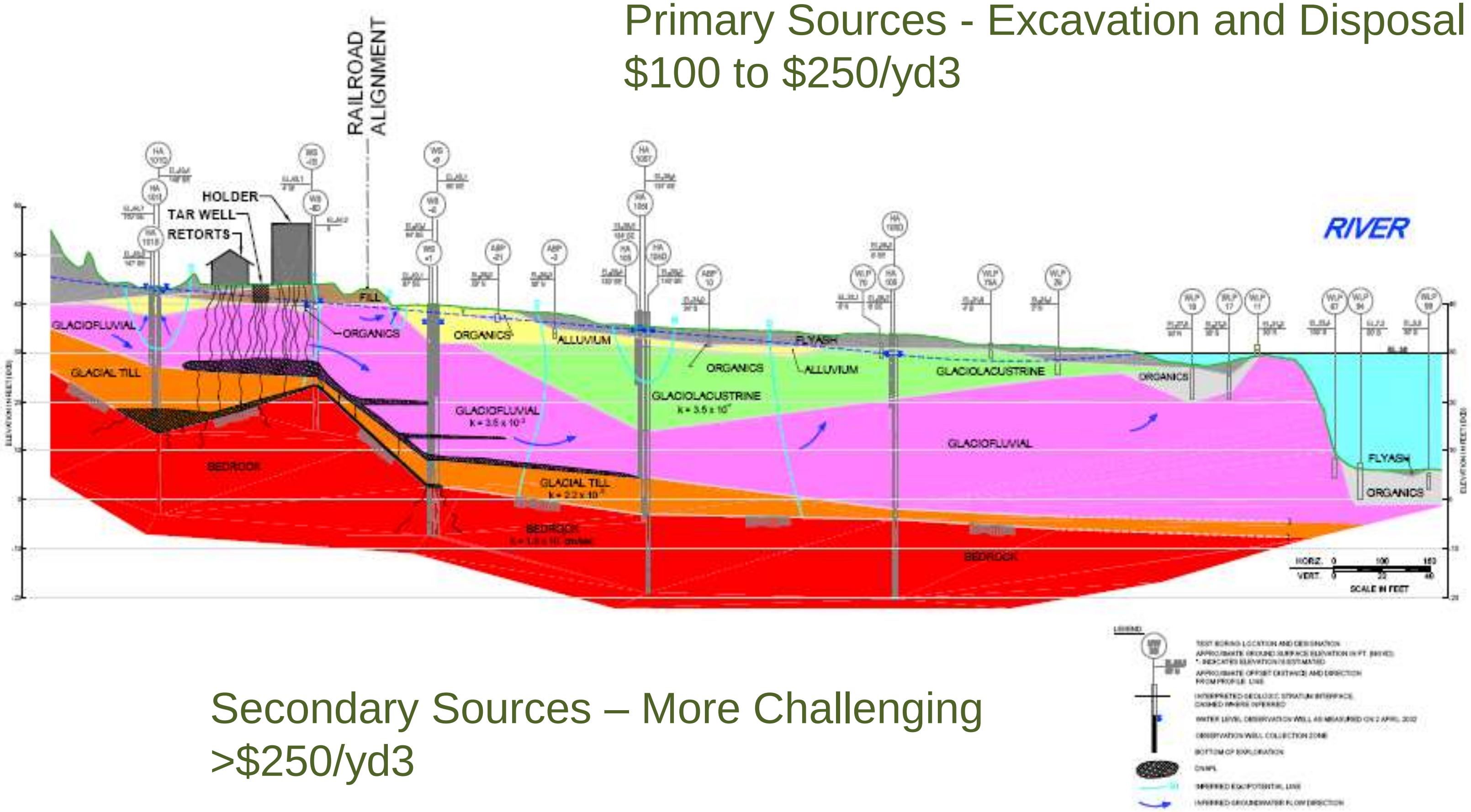
- What is ISGS Technology?
- History of ISGS Technology
- Proof of Concept / Bench Testing
- Field Applications
  - Denver, CO
  - Gainesville, FL
  - Fanwood, NJ
  - Boston, MA
- Geochemical Modeling related to Permanence/Longevity
- Costs
- Questions?

The NAPL Challenge- “Secondary Sources”

Primary Sources - Excavation and Disposal
$100 to $250/yd3



Secondary Sources – More Challenging
>$250/yd3

Contaminant Flux Definition (Enfield, 2001)

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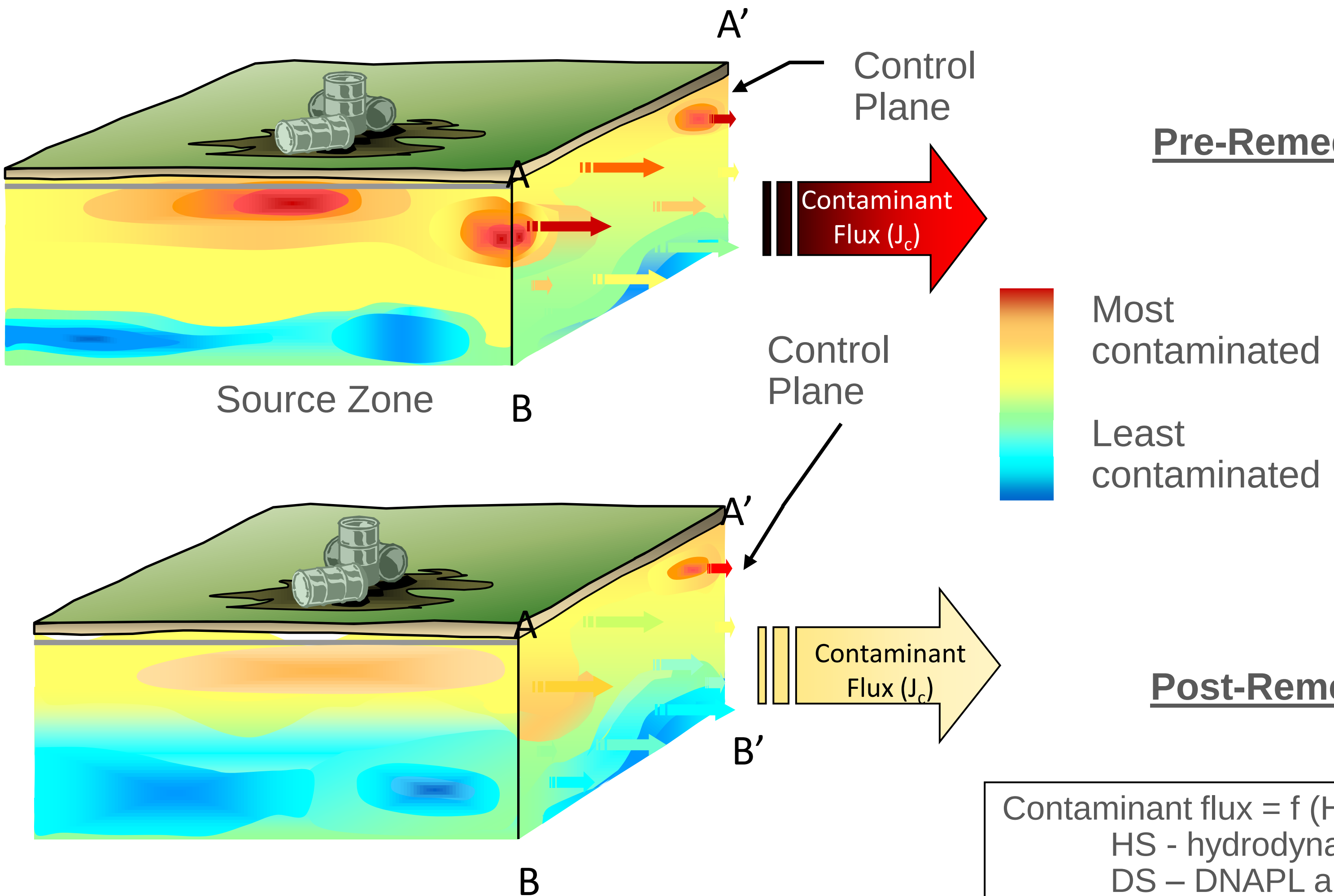


Pre-Remediation:

Post-Remediation:

Contaminant flux = f (HS, DS)
HS - hydrodynamic structure
DS – DNAPL architecture

ISGS™ Chemistry

ISGS solution is a proprietary blend of permanganate and mineral salts that form a stable mineral precipitate

In the presence of an organic compound (R), MnO4 reactions yield an oxidized intermediate (Rox) or CO2 ,… plus MnO2

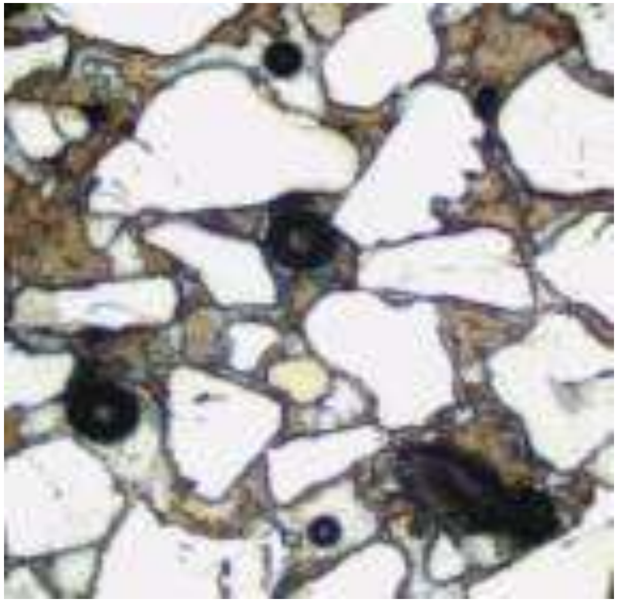
$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \text{ or } Rox$$

ISGS™ Chemistry

- **Reagent Composition:**
  - ➢ Modified permanganate solution
  - ➢ Proprietary combination of cold-water soluble inorganic metals & salts which serve as hardening or concretizing agents

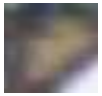
- **Mechanisms of Action:**
  - ➢ Permanganate reacts with dissolved phase organic contaminants:
    - ✓ “Hardening” or "chemical weathering” of residual NAPL
    - ✓ MnO2 generated preferentially in high concentration area surrounding NAPL
  - ➢ Proprietary reagents react with MnO2 to form a stable precipitate
  - ➢ Precipitate rapidly reduces porosity (>80%) and permeability (>90%)

mass removal + reduced NAPL mobility
+ reduced porosity =
flux reduction
(i.e., long-term NAPL stabilization)




Likely NAPL


Soil Grain


ISGS coating


Epoxy
(open pore space)

A New NAPL Management Tool

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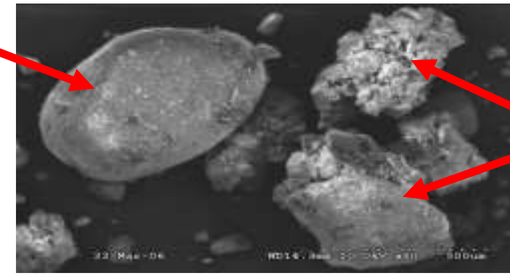
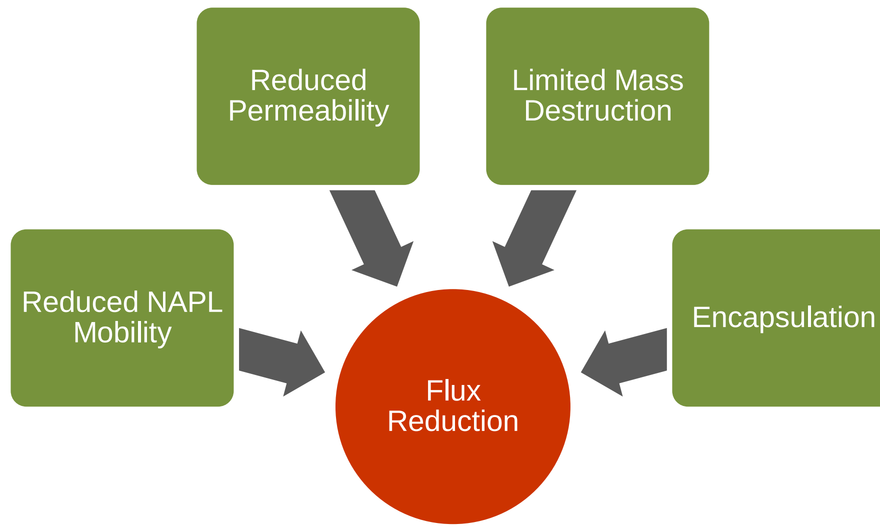
- **ISGS Effects**
  - Creates a stable “crust”
  - Reduces permeability
  - Immobilizes NAPL

NAPL-coated soil grain not exposed to ISGS



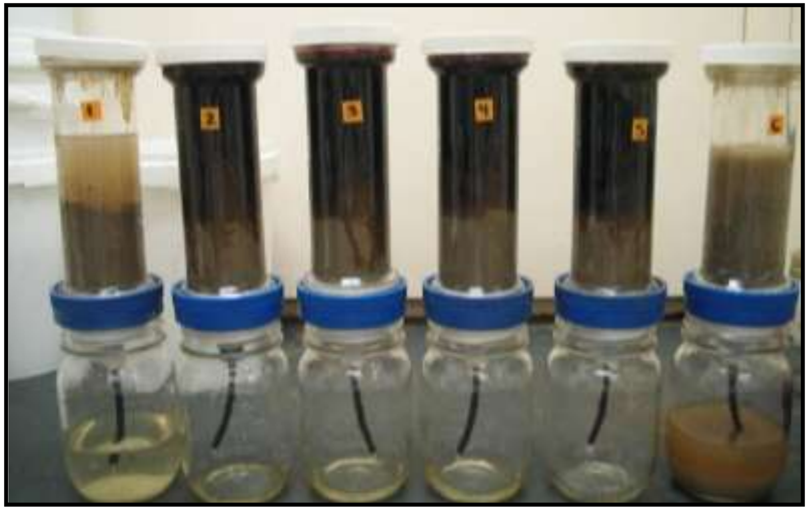
NAPL-coated soil grain exposed to ISGS

- **ISGS Addresses NAPL Challenges**
  - Reduces measurable NAPL
  - Reduces dissolution of NAPL constituents
  - Reduces flux of NAPL into groundwater
  - Enhances natural attenuation of NAPL constituents



ISGS for NAPL Challenges - Advantages

1. Liquid amendment – easy to inject and target source areas.
2. Rapid reactions (days) yield reduced aquifer permeability and COI flux
3. Applicable to wide range of organic and inorganic COIs
4. Only treat a fraction of TOD
5. Long term (crust analyses & geochemical modeling suggest > 100 yr, supported by over 10 yr field data)
6. Relatively low cost for localized source areas
7. Logical alternative to mass removal and mass destruction



Technology Development

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- **1997** Conceptualization / Proof of Concept
- **1998** - 1999 TCE - R&D at UW and Adventus
- **1999 - 2001** Camp Borden (pilot)
- **2002 - 2003** PAHs, PCP – Denver, CO (pilot)
- 2**004** – PAHs – Denver, CO (full scale)
- **2004 –** PAHs, PCP – Gainesville, FL (bench).
- **2005 -** PAHs, PCP - Gainesville, FL (pilot)
- **2007 –** PAHs - MGP NE Utilities (bench)
- **2008 –** PAHs, PCP - Gainesville, FL (pilot)
- **2008 –** PAHs - Creosote works, LA (bench)
- **2009 –** solvents, benzene - plastics manufacturer (bench)
- **2010 –** PAHs - Montgomery, AL (full scale)
- **2010 –** LNAPL – South Boston, MA (bench test)
- **2013 -** LNAPL – Fanwood, NJ (full-scale)
- **2013 –** LNAPL and DNAPL, Frankford, PA (pilot test)
- **2013 –** Creosote and PAHs – Gainesville (full scale)
- **2013 –** Coal Tar and PAHs – Fanwood, NJ

Proof of Concept- Bench Testing

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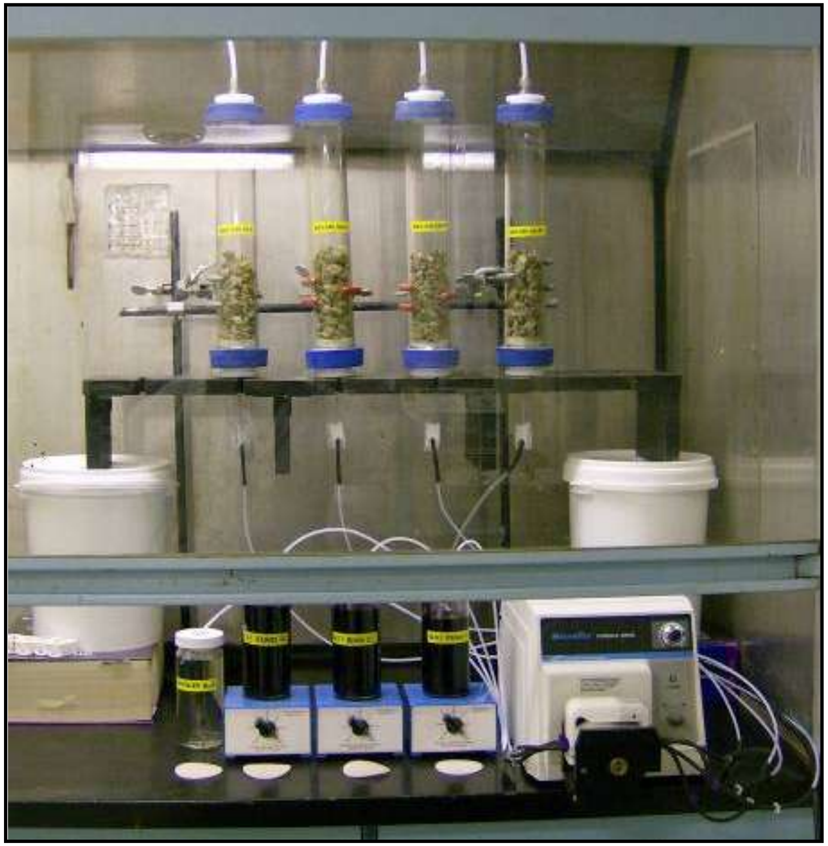

- Saturate w/ISGS reagents
- 20 days reaction time
- Drain
- Run Up-flow Column (DI)
- Compare with Control

Typical Bench Test Results – COIs in Leachate (ca. 7 days treatment time)

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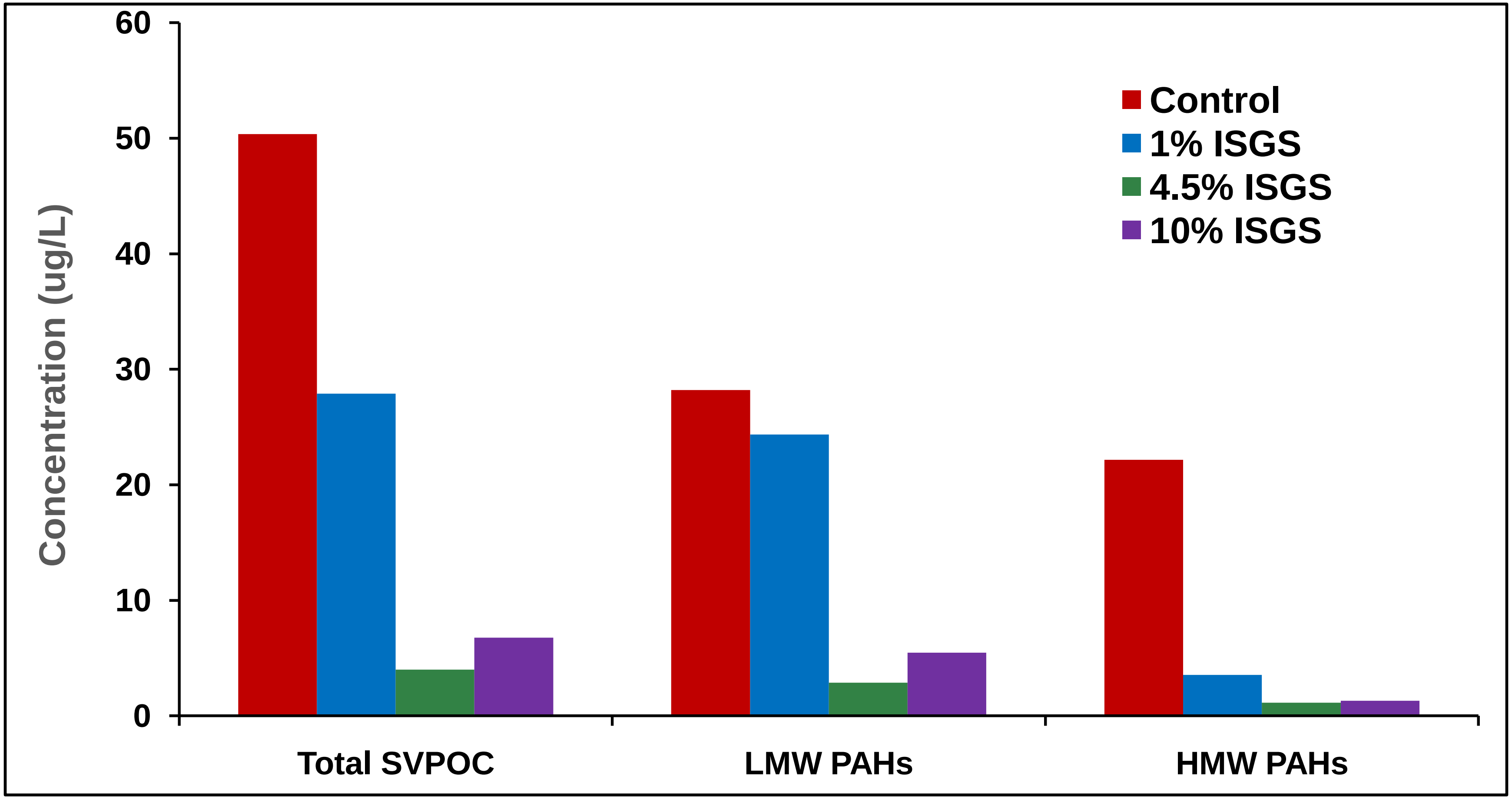

First Full-Scale Application - Denver, CO

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Pre Injection – NAPL Thickness (ft)

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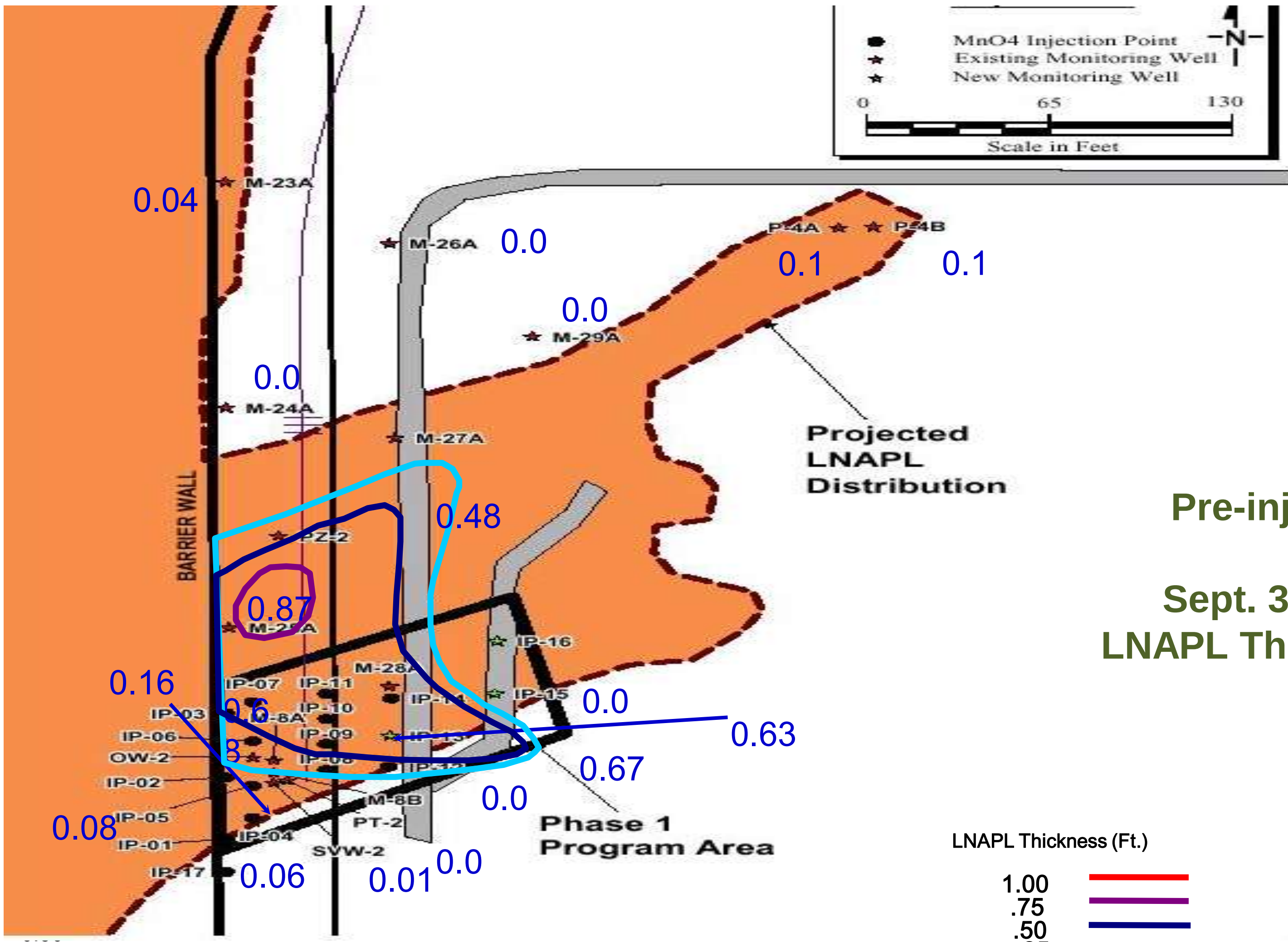

Pre-injection

Sept. 3 2001 –
LNAPL Thickness (Ft)

LNAPL Thickness (Ft.)
1.00
.75
.50
.25

Post Injection – NAPL Thickness (ft)

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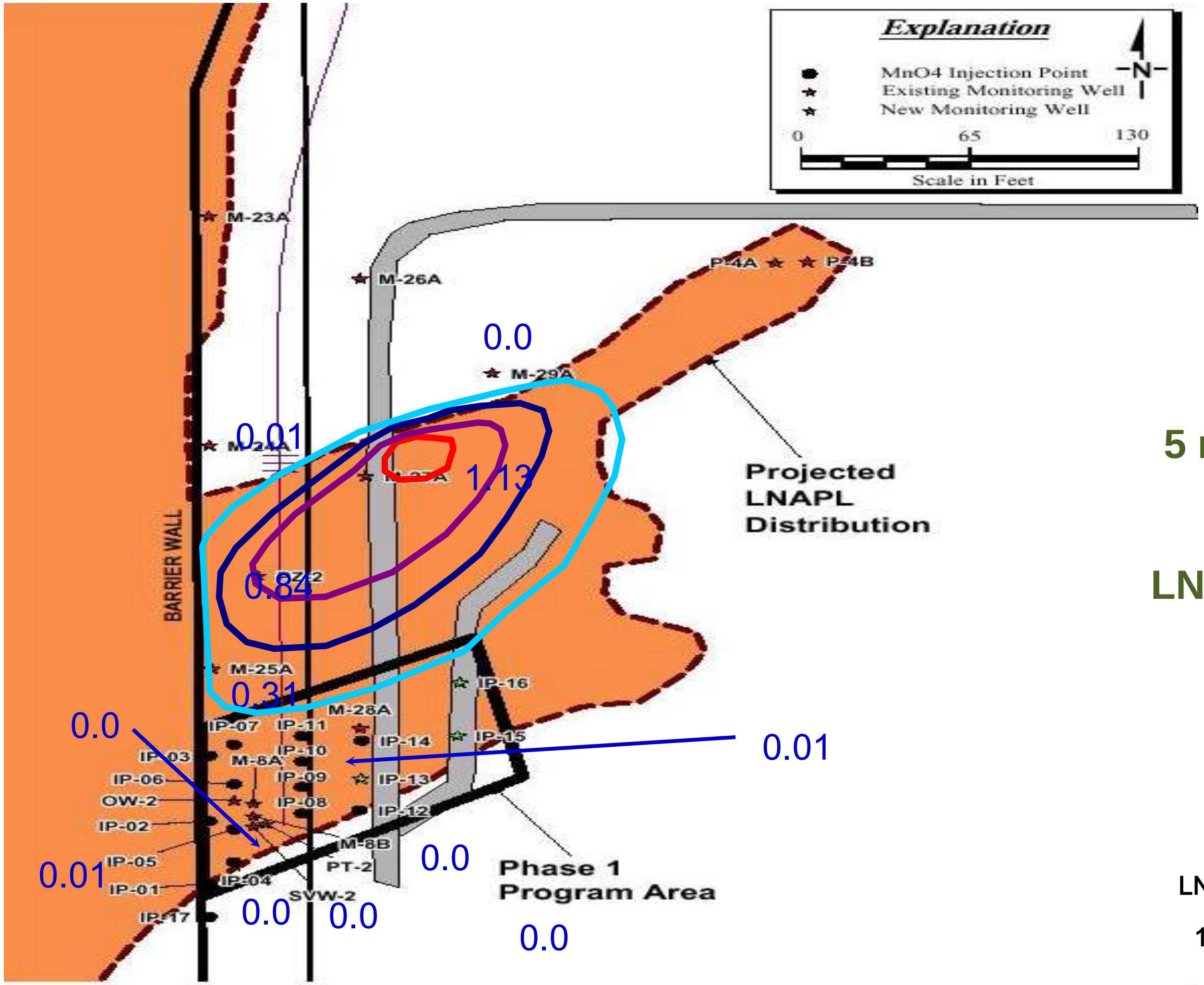

5 months post-injection

Feb. 22, 2002
LNAPL Thickness (Ft)

LNAPL Thickness (Ft.)

1.00

.75

.50

.25

Non-Treated Soil 14 ft bgs

ISGS Treated Soil 14 ft bgs

ISGS ™ - Case Study
Koppers Site, Denver, CO

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Site: Former Kopper's Inc Superfund Site, CO

Application: 24,050 USG of 3% ISGS solution injected into 13 locations

target area = 75 ft x 95 ft x 10 ft

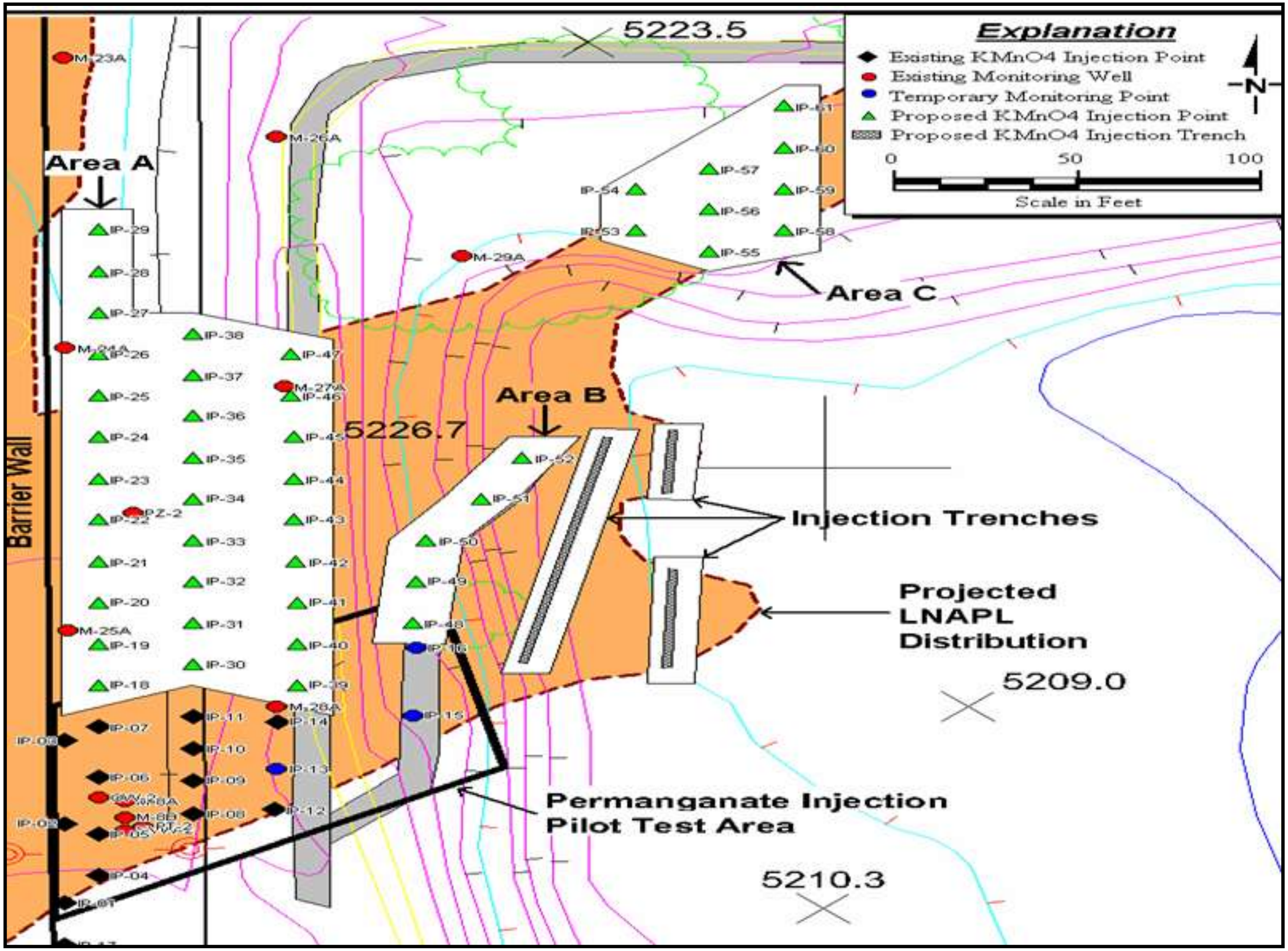
Mass Removal:

COI (mg/kg)	Average (n=4) Background	Average (n=4) Treated	% Reduction
LMW PAHS	7,633.50	5,996.75	21
HMW PAHs	1,961.55	1,744.55	10
TOTAL PAHs	**9,595.05**	**7,771.30**	**19**
* PENTA	236.00	55.67	76
*** TOTAL CPs**	**284.48**	**59.25**	**79**

Flux Reduction:

COI (mg/L)	Average Background	Average Treated	% Reduction
LMW PAHS	34.41	12.75	73
HMW PAHs	6.05	0.11	99
TOTAL PAHs	**40.46**	**12.86**	**79**
* PENTA	18.91	9.66	49
*** TOTAL CPs**	**23.38**	**10.41**	**56**

Phase II ISGS Application (2004)



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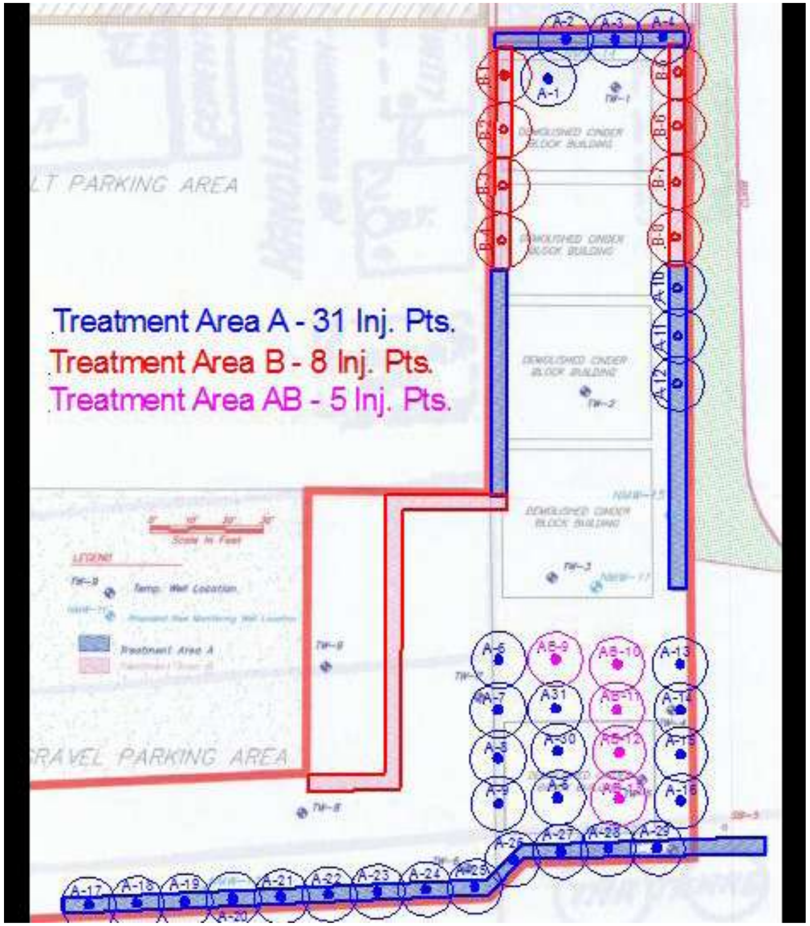
Fanwood, NJ Site

- Historical release of coal tars and heavy ended petroleum compounds.
- The COCs included benzene,naphthalene, Benzo(a)anthracene, Benzo(a)pyrene, and multiple other VOCs and SVOCs.
- The in-situ program covered a total area of 8,955 square feet and treated soil and groundwater from 5-10 ft. below ground surface.
- ISGS solution were injected into 44 points via direct push technologies.
- Two intervals between from 5-7 and 8-10 feet below ground surface (bgs) were used to inject the liquids into the targeted media affecting a radius of 7.5 feet for each point.



Fanwood, NJ Site - Results

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Five monitoring wells were sampled during the baseline sampling event of August 2013 and the first two post-injection sampling events. These wells are: MW-11, MW-12, MW-13, MW-14 and MW-15.

Table 1. CVOC Data for MW-11 (µg/L).

MW-11			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	0.461	0.312	ND 0.10
Benzo(a)anthracene	0.255	0.847	0.146
Benzo(a)pyrene	0.172	0.54	ND 0.10
Benzo(b)fluoranthene	0.218	0.76	ND 0.10
Chrysene	0.166	0.508	ND 0.10
Fluorene	0.791	0.314	0.239
Benzene	67.5	8.4	14.4
Ethylbenzene	6.6	ND 5.0	0.77 J
Toluene	46.5	ND 5.0	3.0
Total Xylenes	19.1	ND 5.0	2.7
Total Alkanes	63 J	ND	ND

Fanwood, NJ Site - Results

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Table 3. CVOC Data for MW-13 (μg/L).

MW-13			
Sampling Date	**08/30/2013**	**10/16/2013**	**01/15/2014**
Acenaphtylene	81.3	11.6	0.64
Benzo(a)anthracene	2.92	0.435	0.684
Benzo(a)pyrene	1.75	ND 0.10	0.192
Benzo(b)fluoranthene	2.24	ND 0.10	0.233
Benzo(g,h,i)perylene	0.698	ND 0.10	ND 0.10
Benzo(k)fluoranthene	0.895	ND 0.10	0.121
Chrysene	2.02	0.235	0.409
Naphthalene	1,920	187	1.18
Benzene	100	48.7	175
Ethylbenzene	43.4	10.4	61.9
Toluene	160	24.4	161
Total Xylenes	179	41.6	171
Total Alkanes	3,625 J	ND	ND

Fanwood, NJ Site - Results

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Free Product Data

Ten different wells were sampled before the implementation of the remedial injection event of September 2013 and the depth of the free product that was present in each well was measured. As Table 6 shows all ten wells appear to have elevated free product levels during the March 2013 baseline sampling event that ranged from 1.22 ft to 5.37 ft.

Table 6. Injection Thickness of Free Product (ft).

Well ID	Sampling Date					
	05/25/2012	**06/07/2012**	**03/14/2013**	**10/16/13**	**10/18/13**	**1/15/14**
TW-1/MW-14	4.16	3.90	4.24	**ND**	**ND**	**ND**
TW-2/MW-15	5.34	4.98	5.31	**ND**	**ND**	**ND**
TW-3/MW-11	5.26	5.12	5.37	**ND**	**ND**	**ND**
TW-4	5.35	5.02	5.11			
TW-5/MW-12	5.60	4.99	4.64	**ND**	**ND**	**ND**
TW-6	4.06	4.02	3.75			
TW-7	5.31	5.08	5.11			
TW-8/MW-13	3.43	3.07	3.26	**ND**	**ND**	**ND**
TW-9	1.15	1.14	1.22			
TW-10	5.02	5.09	4.16			

Fanwood, NJ Site - Results

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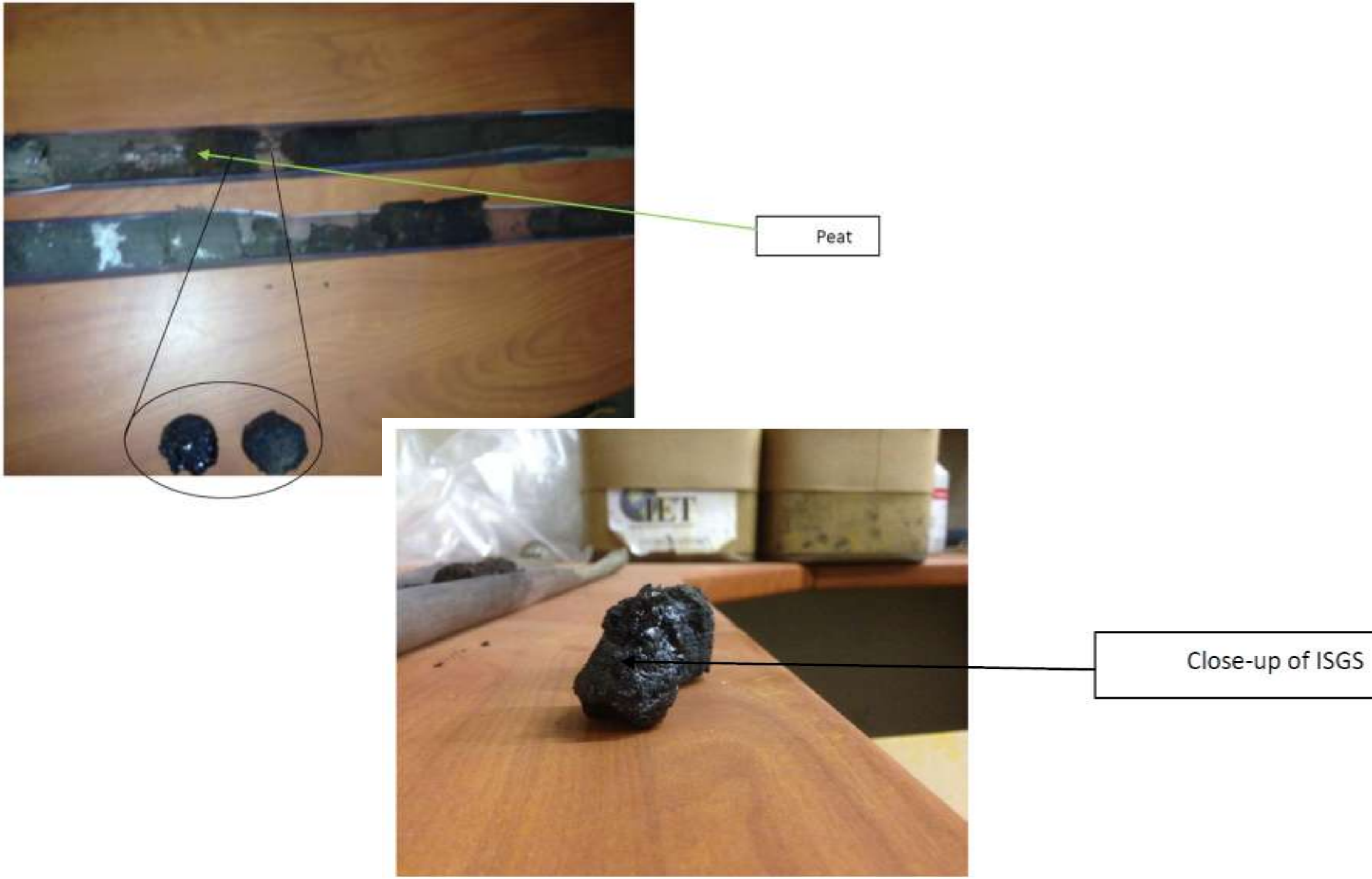
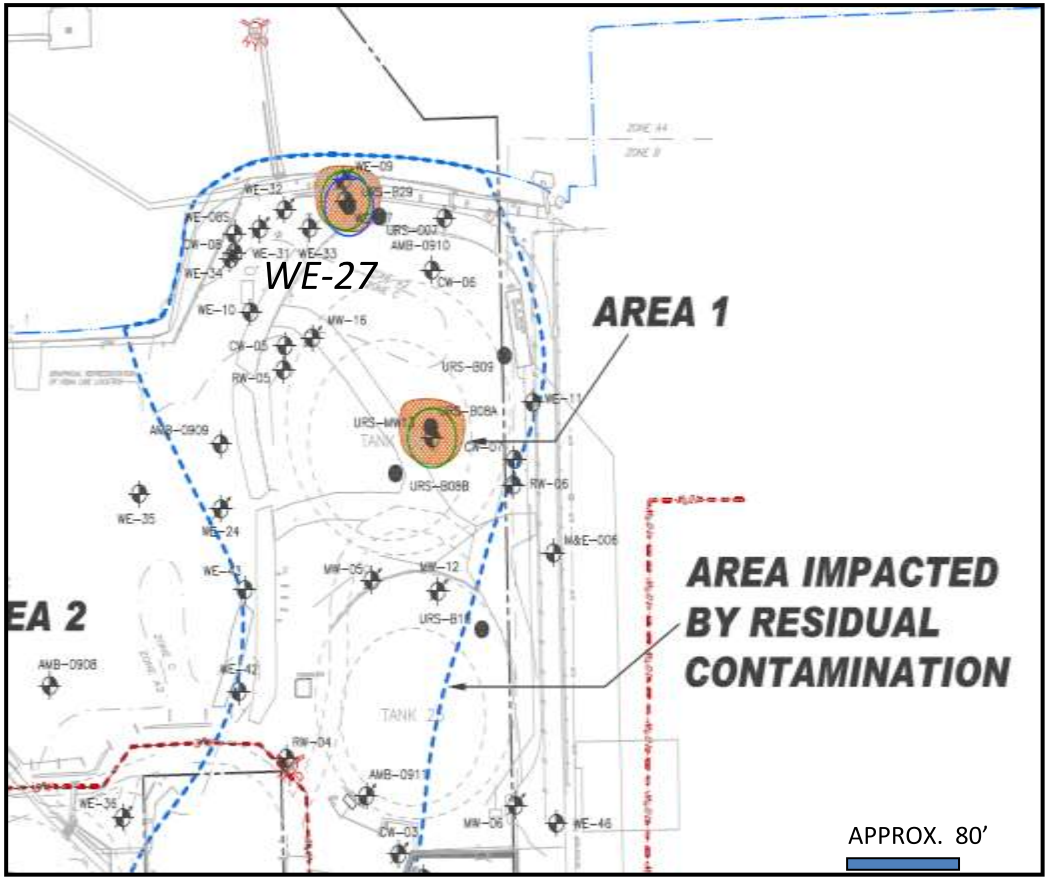


South Boston Site – Bench Test



2009 LNAPL THICKNESS DATA

WE-27 – 0.07' AVG (MAX 0.19')

MW13 – 0.04' AVG (MAX 0.07')

WE-33 – 0.02' AVG (MAX 0.07')

South Boston Bench Test Results

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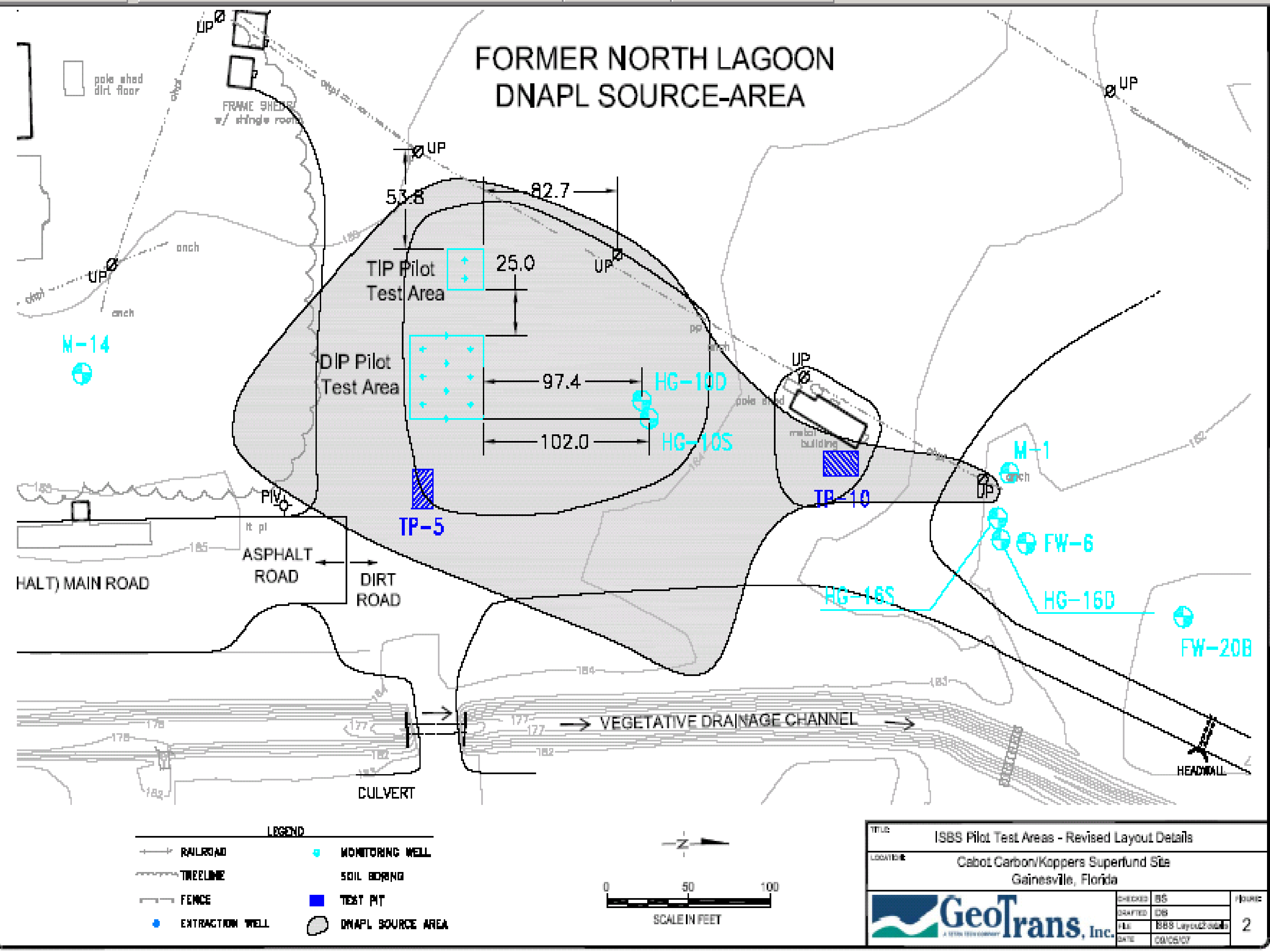
- **Objectives:**
  - Validate ISGS treatment applicability to TPH
  - Identify most cost-effective treatment regime (based on site soil)
- **Method:**
  - batch & column studies
- **Results:**
  - TOD 5 to 8 g/kg (B-Header), 30 to 42 g/kg (WE-27)
  - 60 to 80% reduction in EPH leachate concentrations in 14 days
  - 13 to 30% reduction in EPH soil concentrations in 14 days
  - 44 to 67% reduction in permeability to NAPL and 17% reduction in NAPL fluid saturation
  - ISGS was effective for NAPL stabilization for soils and constituents at this site
  - 4.5% ISGS solution was recommended for full-scale

Cabot Carbon / Koppers Superfund Site, Gainesville, FL

- 90 acre site
- Pump & treat in place
- Secondary NAPL issues


FORMER NORTH LAGOON
DNAPL SOURCE-AREA
TIP Pilot
Test Area
DIP Pilot
Test Area
53.8
82.7
25.0
97.4
102.0
HG-10D
HG-10S
TP-5
TP-10
M-14
M-1
FW-6
HG-16S
HG-16D
FW-20B
UP
pole shed
dirt floor
FRAME SHED
w/ shingle roof
metal building
PIV
ASPHALT
ROAD
DIRT
ROAD
HALT) MAIN ROAD
VEGETATIVE DRAINAGE CHANNEL
CULVERT
HEADWALL
LEGEND
RAILROAD
TREELINE
FENCE
EXTRACTION WELL
MONITORING WELL
SOIL BORING
TEST PIT
DNAPL SOURCE AREA
0
50
100
SCALE IN FEET
TITLE:
ISBS Pilot Test Areas - Revised Layout Details
LOCATION:
Cabot Carbon/Koppers Superfund Site
Gainesville, Florida
GeoTrans, Inc.
CHECKED BS
DRAFTED DB
DATE 09/05/07
FIGURE
2

Results - NAPL Monitoring Wells

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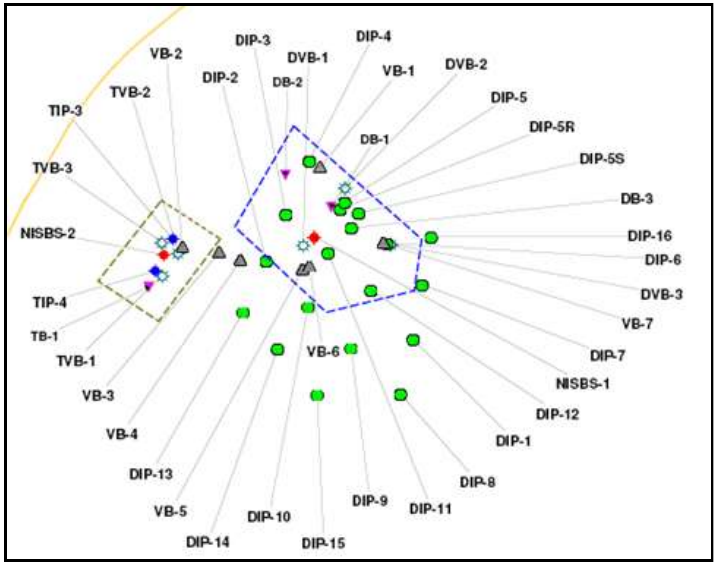
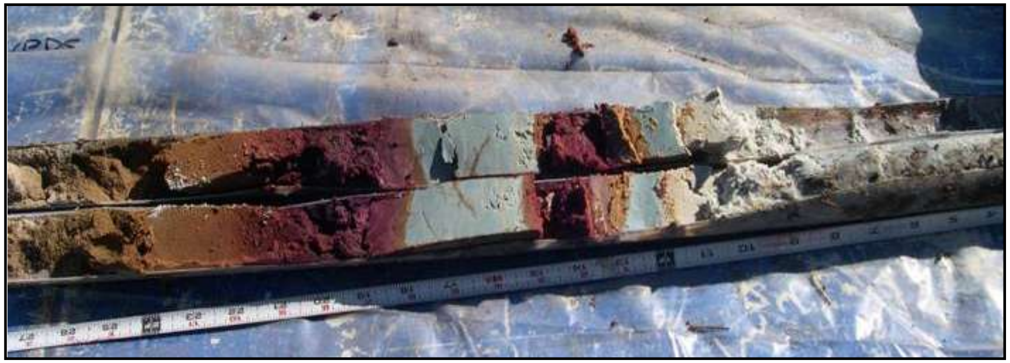
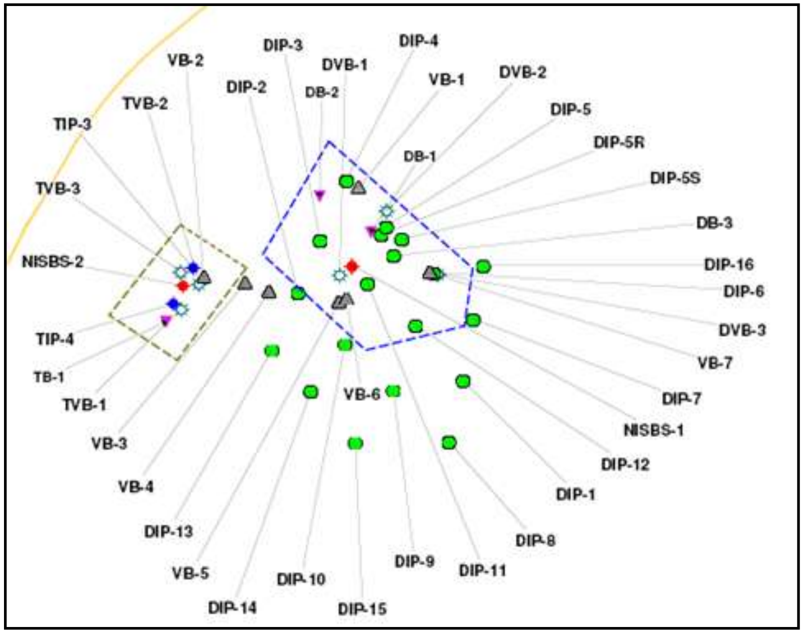




1 week Post ISGS treatment =
no measurable free-phase NAPL in any of the monitoring wells.

Monitoring Well	Pre-Injection	Post-Injection
NISBS- 1	NAPL	stain
NISBS-2	NAPL	stain
TIP-3	ND	ND
TIP-4	ND	ND
UGH Recovery	NAPL	No NAPL

Results -Total PAH Concentrations in Soil and in Leachate



6 cores (3 sections) before treatment

6 cores (2 depths) after treatment

Best matched cores (SOIL):
dropped from 7,250 mg/kg to 3,600 mg/kg

Best matched cores (LEACHATE):
dropped from 11,700 mg/L to 560 mg/L

PAH concentrations in soil reduced by up to 50% within 3 months.

PAH leachate concentrations reduced by up to 98% within 3 months.

ISGS Field Data – Decrease in K_h Values
Woodward Coke Site – Dolomite, AL

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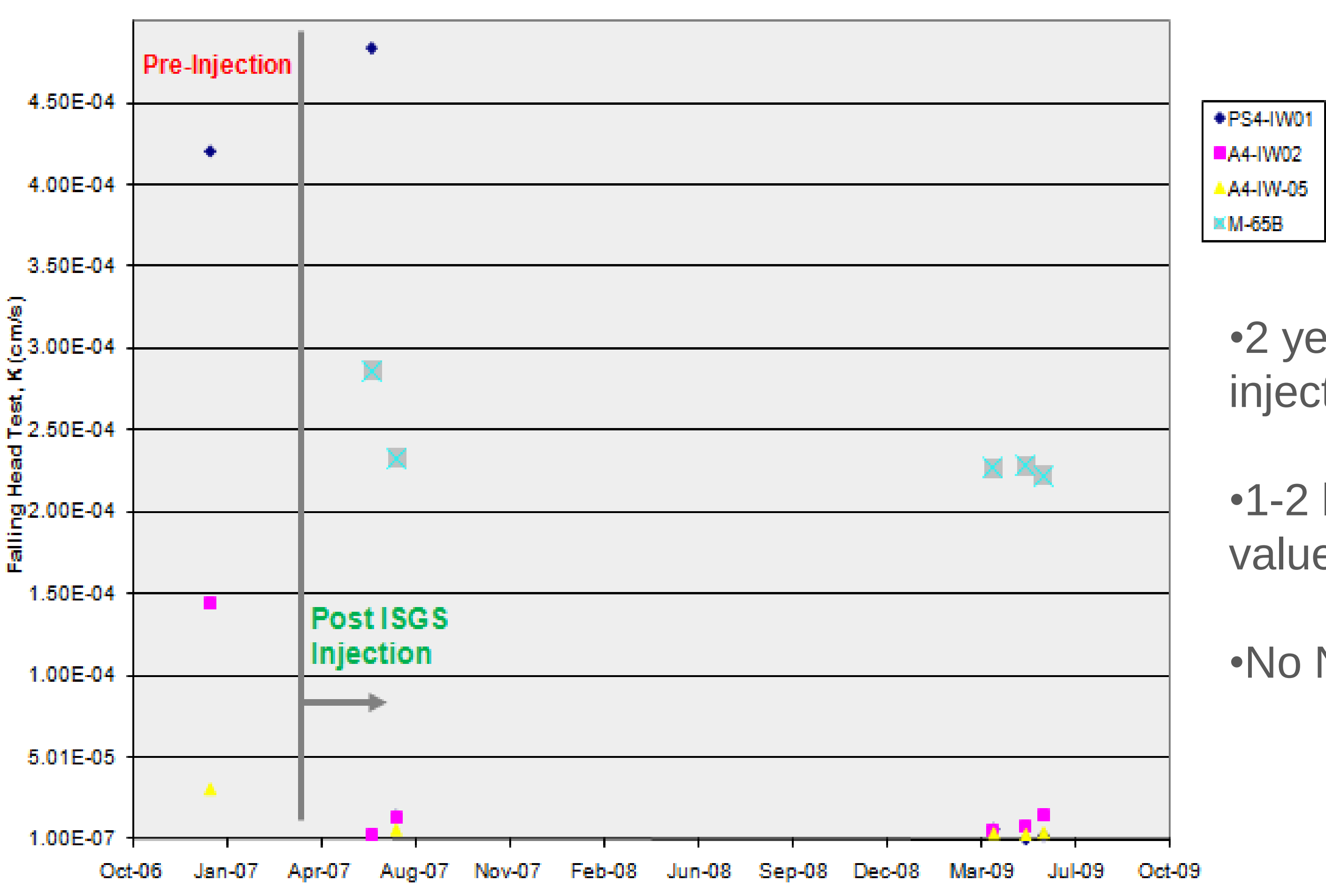
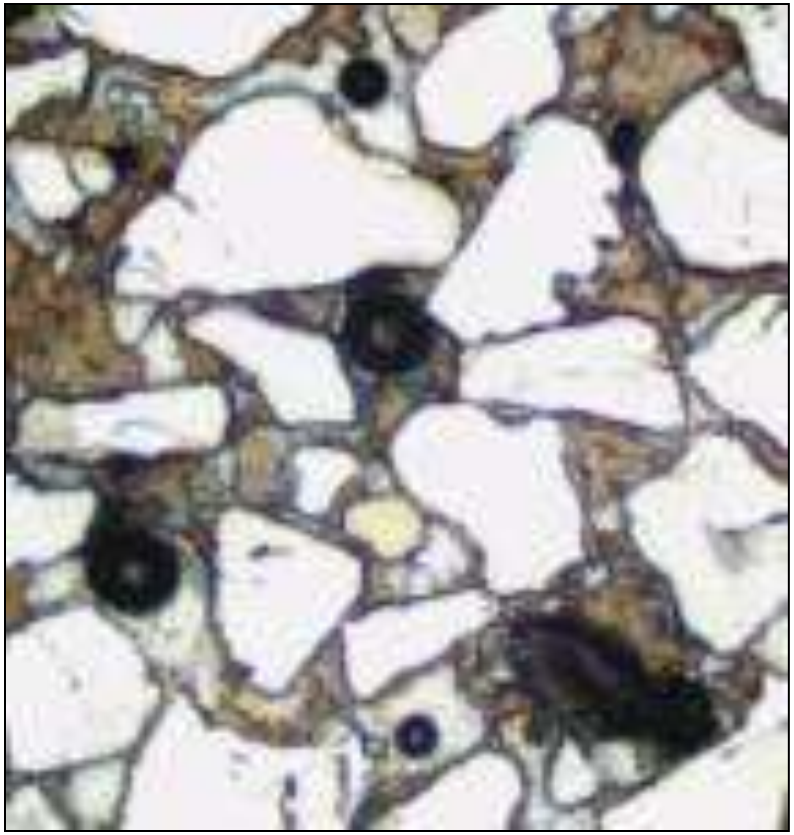
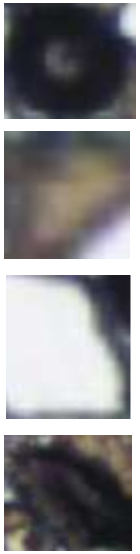


- 2 years post ISGS injection
- 1-2 log decrease in values
- No NAPL in MW

Treated Soil Core Close-up Showing ISGS “Crust” or Coating and NAPL Ganglia





Likely NAPL

ISGS coating

Soil Grain

Epoxy (open pore space)

Conclusion: Soil grains and NAPL blobs coated with ISGS crust

Birnessite is an oxide of Mn and Mg along with Na, Ca and K with the composition: (Na,Ca,K)(Mg,Mn)$Mn_6O_{14}.5H_2O$

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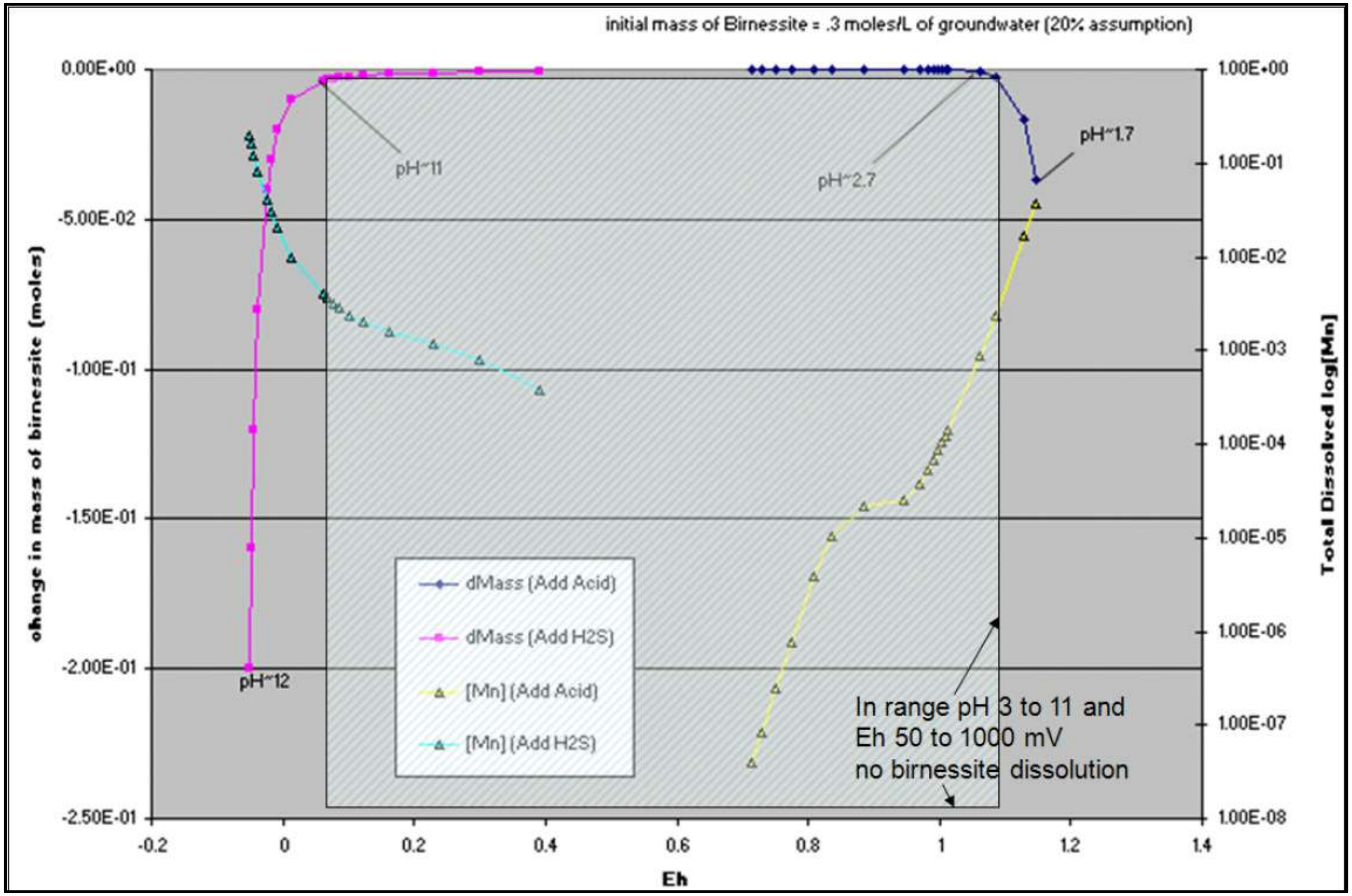
Permanence and Monitoring

- Crust Longevity
  - Crust weathering is dependent on changes in Eh and pH
  - Conduct mineralogy assay
  - Validate using geochemical modeling
- Performance Monitoring
  - Eh, pH for crust stability
  - Permeability tests for flux reduction
  - NAPL fluid saturation

Geochemical Modeling of the Crust



Crust Longevity

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- Back of the envelope calculations suggest crust life ~ 400 years.
- This may be over-estimated because it assumes Eh (-400 mV) and pH (6) at which birnessite is sparingly soluble

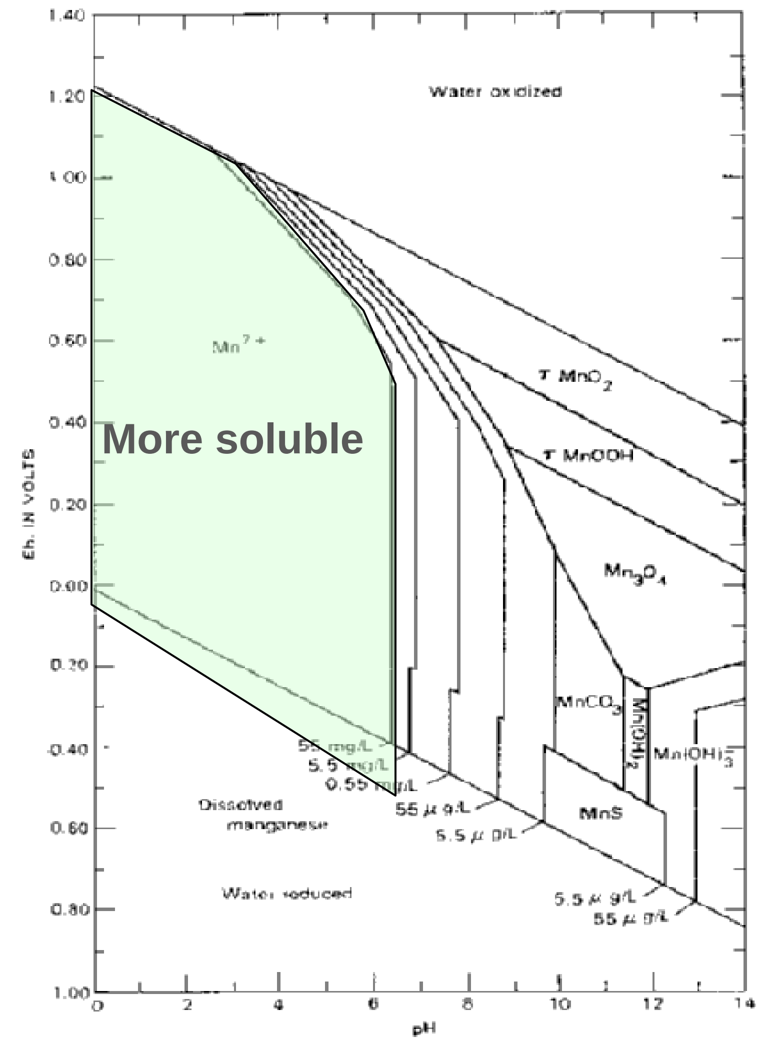

Figure 16. Fields of stability of manganese solids and equilibrium dissolved manganese activity as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, and carbon dioxide species 61 mg/L as HCO_3^-.

Eh-pH diagram from Hem (1985)

Representative Experience
ISGS – Creosote and Related Sites

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Site	COI / Environmental Setting	ISGS Approach / Status
Active Wood Treating Site Superfund Site Denver, CO	**Phase separated creosote (PAHs) and pentachlorophenol (penta). Consolidated shallow alluvium.**	**KMnO4 (no catalysts; no buffer) successful bench and pilot studies completed; full-scale application completed 2004.**
(Active) Wood Treating Site Superfund Site Gainesville, FL	**Phase separated creosote (PAHs). Sand silt environment, 5 to 22 ft bgs.**	**NaMnO4 (catalyzed, buffered) completed bench-scale engineering optimization tests; Pilot-scale technology validation performed in January 2008. 2012 Full-scale application recommended as part of the ROD – installation 2013 to 2015.**
Former Wood Treating Site Montgomery, AL	**Phase separated creosote (PAHs)**	**Field Scale application completed 2009. One to two orders of magnitude reduction in permeability.**
Former Wood Treating Site Cape Fear, NC	**Phase separated creosote (PAHs)**	**Conceptual design completed.**
Former American Creosote Works Winnfield, LA	**Phase separated creosote (PAHs)**	**Engineering optimization bench work completed.**
Former Wood Treating Site Sand Point, ID	**Phase separated creosote (PAHs)**	**Engineering optimization bench work completed; Field Pilot Completed Q3 2010.**
Former Wood Treating Site Netherlands	**Phase separated creosote (PAHs)**	**Engineering optimization bench work completed. Field Pilot pending**

ISGS Material Cost – Field Applications

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Denver, CO	Dolomite, AL	Gainesville, FL
TOD = 18 g/kg	TOD = 1 g/kg	TOD = 122 g/kg
Dense Alluvium $KMnO_4$ @ 4.5 g/kg Injection Wells	Fractured Karst RemOx EC Push-Pull	Sand/Silt RemOx EC Direct Push and Injection wells
1,273 m^3 soil 3% solutions 1,850 USG/IP 2-5 gpm (20 psi)	1,500 m^3 soil 1% solutions 20,000 USG 13 gpm (20-50 psi)	1,415 m^3 soil 4.5 % solutions 620 USG/DIP 2-5 gpm (<50 psi)
Cost = \$40 - 50/m^3 \$31 - 38/yd^3	Cost = \$45 - 50/m^3 \$34 -38/yd^3	Cost = \$60 - 75/m^3 \$50 -60/yd^3

The amount of ISGS reagent required for a given site has a significant influence on project cost. Typical **material costs** range from \$13/yd^3 to \$53/yd^3.

Questions?