John Mousa

From:	Hutton, Richard H [HUTTONRH@gru.com]
Sent:	Monday, May 10, 2010 4:30 PM
To:	Brett P. Goodman; 'chaffins.Randall@epa.gov'; Chris Bird; Greg Council; Helton, Kelsey; Jim Erickson; John Mousa; John Herbert; 'kevin koporec'; Miller.Scott@epamail.epa.gov; Mitchell Brourman (mitch.brourman@hanson.biz); Osteen.Bill@epamail.epa.gov; Richard E. Jackson; Robin Hallbourg; RWCLEARY@aol.com; Stanley Feenstra; wayne_reiber@cabot-corp.com
Subject:	RAOs and Performance Metrics for ISGS
Attachments:	GRU_ACEPD Koppers Performance Objectives.pdf; UW Creosote Emplaced Source Data.pdf; DenI_PermangRmdy_071509.pdf

Scott,

Per your request GRU in concert with ACEPD have developed preliminary proposed performance metrics for assessing the performance of ISGS, or other in-situ solidification remedies for the Koppers Gainesville, FL site. As we have stated previously we have on-going concerns regarding the ability of ISGS achieve the required performance. Please see the attached documents. We appreciate the opportunity in providing input to this process. We feel that more discussion with EPA, Beazer, FDEP, ACEPD & GRU are necessary to better refine these metrics.

Best Regards

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GRU & ACEPD
Proposed Performance Metrics for ISGS
Koppers Gainesville, Florida Superfund Site
May 10, 2010

Purpose

USEPA asked Gainesville Regional Utilities (GRU) to provide preliminary “first cut” recommendations of remedial action objectives (RAO)s and performance metrics that could be included in the record of decision to measure the effectiveness of In-Situ Geochemical Stabilization (ISGS), and to ensure that effectiveness would be attained/maintained over the life of the remedy. This document provides preliminary recommendations for remedial action objectives and performance metrics which would apply to ISGS, or to other technologies (such as In-Situ Soil Stabilization (ISSS)) to remove or immobilize DNAPL at the Koppers Gainesville Superfund Site. It also expresses specific concerns GRU and the Alachua County Environmental Protection Department (ACEPD) have with regard to the potential use of ISGS to treat creosote DNAPL source zones at the Koppers Gainesville site.

While GRU and ACEPD staff and consultants have no experience specifically using ISGS we offer the following opinions regarding objectives and metrics based on our experience conducting remediation at other sites using other methods. We would welcome the opportunity to discuss our thoughts with EPA, Beazer, and Beazer’s consultants regarding these matters.

Background

GRU and ACEPD believe that a critical RAO for this site should be to reduce the mobility, volume, and toxicity of DNAPL to the extent practicable. More specific performance objectives should be to treat or remove DNAPL in the surficial aquifer (SA) and Upper Hawthorn Group (UHG) source zones to (1) immobilize DNAPL to reduce potential <u>downward</u> and lateral mobility of DNAPL; and (2) reduce dissolution and flux of dissolved phase constituents from the DNAPL into the groundwater.

The complexity of the site geology and the depth and extent of creosote DNAPL migration at the site will test the limits of any remedial technology that EPA selects – especially in the Hawthorn Group (HG). It will be critical that adequate performance metrics and an effective monitoring network are in place to ensure that the remedy is in fact meeting remedial action objectives and performance objectives – regardless of the remedial technology that EPA selects.

As we understand it, EPA is considering alternatives for treating the DNAPL in-place in the Surficial Aquifer (SA) and Upper Hawthorn Group (UHG). ISGS and ISSS are leading candidates. ISGS has not been extensively demonstrated, and we continue to have concerns regarding its effectiveness, which are further elucidated later in this document. Overall, we consider that ISSS has been applied more widely and would yield more predictable and long-lasting treatment. Therefore, we prefer ISSS as the lead alternative if it can be employed to effectively solidify the source areas present in the SA and UHG.

Specific Concerns Regarding ISGS

As indicated previously in this document and in CITY OF GAINESVILLE AND ALACHUA COUNTY COMMENTS ON THE AUGUST 2009 (DRAFT) FEASIBILITY STUDY OF REMEDIAL ALTERNATIVES WORKING COPY FOR STAKEHOLDER REVIEW FOR THE CABOT CARBON/KOPPERS SUPERFUND SITE (dated November, 2009), we continue to have concerns regarding the predictability and capability of ISGS to meet performance objectives. Our concerns include the following:

1. **Limited demonstration of technology**. The Denver Koppers site is the only reported field study. We have not seen rigorous presentation of the data from this study (the only documentation we have is Beazer July 15, 2009 PowerPoint presentation). The other 2 known studies reported by Adventus are the Gainesville pilot study and the Waterloo research, both of which showed limitations;

2. **Incomplete Sweep of Gainesville Pilot Test Site by ISGS Solution.** The pilot study at Gainesville Koppers site did not demonstrate success. It showed poor sweep of the ISGS solution through the test section, in fact areas < 10 ft from the injection wells showed no MnO_2 coverage, the solution sank to the bottom of the treatment zone thereby failing to contact shallow DNAPL and did not cause consistent reduction in dissolved phased contaminant concentrations;

3. **Ability of ISGS to treat the interior of continuous DNAPL masses and to stop vertical DNAPL migration.** ISGS solutions will react with the surface of the DNAPL body (at the water-DNAPL interface). The interior of a DNAPL body (ganglia, pool, or continuous DNAPL stringer) will not be treated. Where DNAPL is migrating, the ISGS treatment could leave a hollow tube of treated DNAPL inside which mobile DNAPL could continue to flow.

4. **Longevity of precipitate/prevention of rebound.** The Adventus May 2009 White Paper on ISGS references University of Waterloo (Dr. Neil Thomson) research as a demonstration of the success of ISGS. However, research by Thomson, N.R., et al (2008) showed rebound of dissolved-phase creosote compounds within 4 years of application of $KMnO_4$ at a creosote test plot (see attached figure)[1];

5. **Increase in dissolved phase PAHs.** The Denver study showed a 434% increase in core leachate PAHs after treatment with ISGS (page 11, slide 22 of Beazer July 15, 2009 presentation, attached). Beazer's own

conclusions at the end of the slide presentation concede that the effects on dissolved-phase groundwater concentrations downgradient of the ISGS treated area are undetermined at this time (page 12, slide 24 of Beazer July 15, 2009 presentation, attached). The overall objective of the remedy must include the treatment of such dissolved-phase PAHs.

6. **Documenting Reduction of DNAPL Mobility** We believe that the rate at which DNAPL flows into monitoring wells should decline dramatically if ISGS (or ISSS) successfully reduces DNAPL mobility. However, we believe that is not likely to be a reliable indicator of reduced DNAPL mobility (because so few monitoring wells exist in the source areas and significant volumes of DNAPL could continue migrating undetected elsewhere). We are unsure how to properly quantify reduced DNAPL mobility.

All of these concerns need to be considered and addressed in deciding the suitability of ISGS and in designing and implementing ISGS if it is used.

Performance Metrics

Given the absence of any successful demonstration of ISGS in the field, we are uncomfortable with suggesting specific performance metrics for measuring the successfulness of ISGS treatment. Materials provided by Beazer assert that ISGS will result in the following effects:

- (i) DNAPL is chemically weathered;
- (ii) A manganese dioxide coating/shell physically forms around the DNAPL;
- (iii) There is a material reduction in DNAPL recovery in existing DNAPL recovery wells; and
- (iv) There is a reduced flux of dissolved phase constituents of interest in groundwater flowing through the DNAPL areas.

At a minimum, Beazer should be required to establish, based on pre- and post-treatment DNAPL area sampling, that all of these effects are occurring throughout the DNAPL source areas. GRU and ACEPD do not have specific experience with ISGS such that we can recommend specific techniques to assess the chemical weathering and manganese dioxide coating formation. We suggest that Beazer and its consultants propose such techniques, which should be reviewed by EPA and stakeholders, and included in the ROD.

Beazer should be required to establish a material reduction in the flux of dissolved phase constituents of interest in groundwater flowing through the DNAPL areas. Later in this document we describe flux monitoring devices which could be used to assess this.

The ultimate objective of any remedy implemented at the site must be that groundwater will meet Florida Groundwater Cleanup Target Levels (GCTLs) at the property boundary within a reasonable period of time and upon termination of any hydraulic control that is required during implementation of the remedy. To establish that this result has been obtained, it will be necessary to have an effective monitoring network and protocol for duration of the remedy. At a minimum, we believe the following should be included in a monitoring plan:

1. New monitoring wells should be installed in the SA and UHG around the perimeter of the source areas to be treated. Lower Hawthorn group (LHG) wells should be installed at or near the South Lagoon and Process Areas where wells in the LHG do not exist now (Existing UHG and LHG wells near the North Lagoon and Drip Track should be retained). These wells should be installed inside the slurry wall or other containment a short distance from the treated areas. They should be installed before treatment, and should be sampled before, during and after treatment until Beazer can effectively establish that GCTLs are met in groundwater at the property boundary. Given the rebound evidence presented in the Thomson study, it will be important to require several years of monitoring even after GCTLs are initially met in groundwater at the property boundary;

2. The SA IRM trenches should continue to be pumped and monitored for flow and constituent concentrations to monitor the changes in contaminant mass discharge from the treated source zones until it is conclusively demonstrated that the treatment by ISGS or ISSS is successful. In the case of ISGS this must include the appearance of the purple color of the permanganate solution in the IRM trenches indicating widespread flooding of the SA. Note: there will be a need to continuously maintain hydraulic control within the slurry walled area of SA and UHG until Beazer can demonstrate that groundwater meets GCTLs at the property boundary and will continue to meet GCTLs following termination of hydraulic control within the slurry wall;

3. The wells described above (Item 1) and trenches should be monitored for water levels and ISGS reagent during treatment. They should be monitored for constituents of concern and water levels before, during and after treatment, and periodically on a long-term basis. The addition of a conservative tracer with the ISGS solution, such as bromide, should also be considered;

4. Installation of mass flux monitoring devices in the source zone perimeter wells, such as those developed by Mike Annable of University of Florida, should be considered. Passive flux meters (PFMs) developed at the University of Florida use “a sorptive permeable medium placed in either a borehole or monitoring well to intercept contaminated groundwater and release "resident" tracers. The sorbent pack is placed in a groundwater flow field for a specified exposure time and then recovered for extraction

and analysis. By quantifying the mass fraction of resident tracers lost and the mass of contaminant sorbed, groundwater and contaminant fluxes are calculated." The PFM is described at http://www.ncbi.nlm.nih.gov/pubmed/16201648 and in several papers at http://www.clu-in.org/contaminantfocus/default.focus/sec/Dense_Nonaqueous_Phase_Liquids_(DNAPLs)/cat/Detection_and_Site_Characterization/p/0i

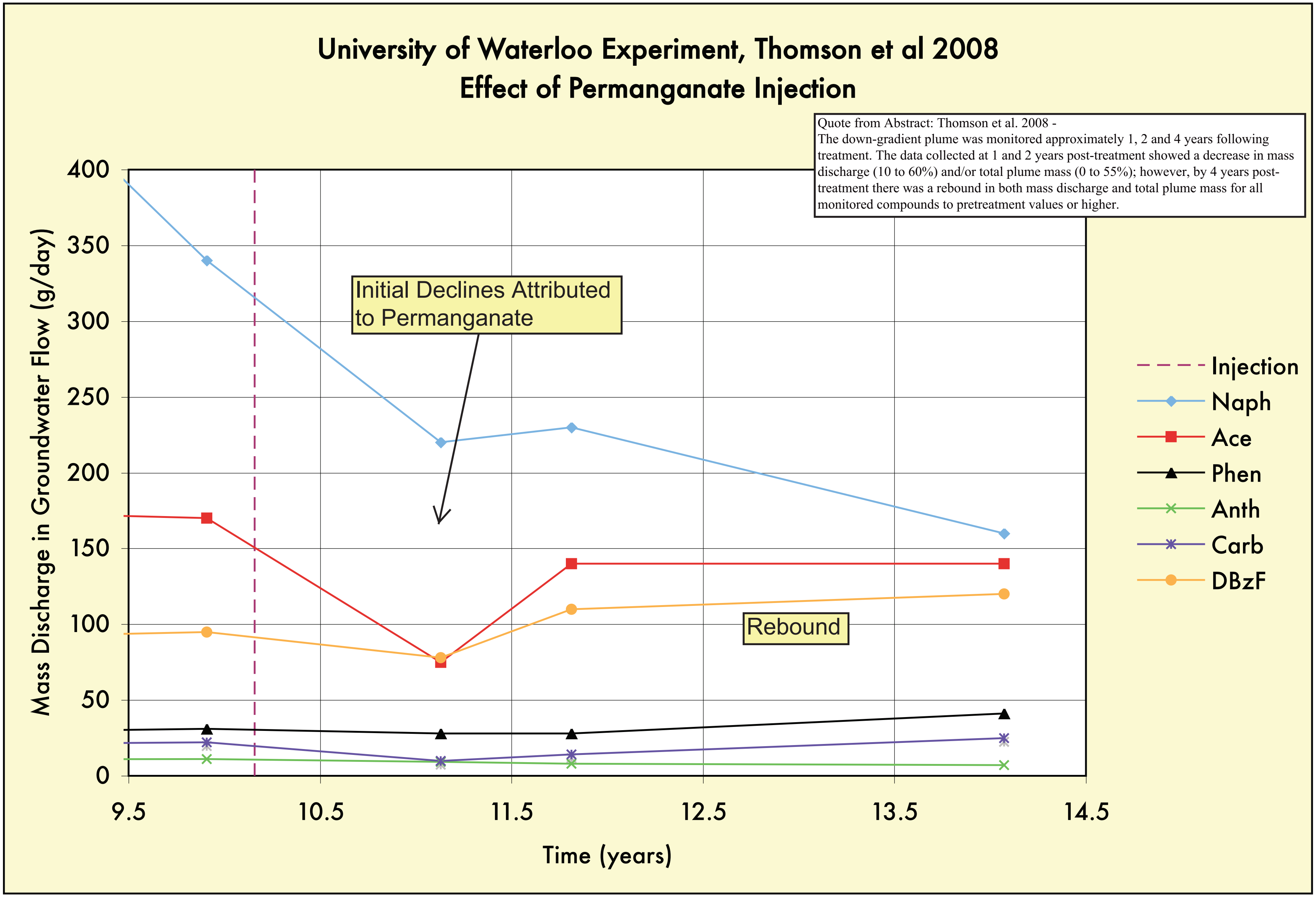
5. All existing source zone perimeter wells (SA, UHG and LHG) and trenches within the slurry wall should show pronounced decreases in dissolved phase contaminants which do not rebound[1]. An appropriate goal for wells within the slurry wall would be to meet FDEP Natural Attenuation Default Source Criteria. This is appropriate because groundwater inside the slurry wall may move vertically downward into the UHG or LHG. Contaminant mass discharge measured from the IRM trenches should decline as a result of reduced dissolved concentrations or reduced groundwater flow, or both, from the source zones. Mass discharge should also be calculated based on well concentration and water level data;

6. The amount of DNAPL bailed from HG wells should continue to be tracked. To provide evidence that treatment is successful, the amount of DNAPL collected should sharply decline;

7. All monitoring wells beyond the source zone perimeter wells (inside and outside the slurry wall, but within the property boundary) should show stable or declining contaminant concentrations. Existing monitoring wells should be retained or replaced so groundwater response to the remedial actions can be measured.

8. All monitoring wells at property boundary and off-site should meet Florida GCTLs within reasonable pre-defined timeframes. For the Floridan Aquifer and SA, this should be achieved as soon as possible. The HG will likely require several years after implementation of the final remedy to achieve GCTLs.

Note:
[1]We have concerns about rebound of concentrations over time, based on research by Thomson, et. al (2008). It is important to monitor all of the source zone perimeter wells on a long-term basis to ensure this is not occurring. We understand that the current ISGS formulation includes aluminum silicates and other components that were not used in the Thomson study. However, there has been no demonstration that this newer formulation will prevent rebound.



University of Waterloo Experiment, Thomson et al 2008
Effect of Permanganate Injection
Quote from Abstract: Thomson et al. 2008 -
The down-gradient plume was monitored approximately 1, 2 and 4 years following treatment. The data collected at 1 and 2 years post-treatment showed a decrease in mass discharge (10 to 60%) and/or total plume mass (0 to 55%); however, by 4 years post-treatment there was a rebound in both mass discharge and total plume mass for all monitored compounds to pretreatment values or higher.
Initial Declines Attributed to Permanganate
Rebound
Mass Discharge in Groundwater Flow (g/day)
400
350
300
250
200
150
100
50
0
9.5
10.5
11.5
12.5
13.5
14.5
Time (years)
Injection
Naph
Ace
Phen
Anth
Carb
DBzF

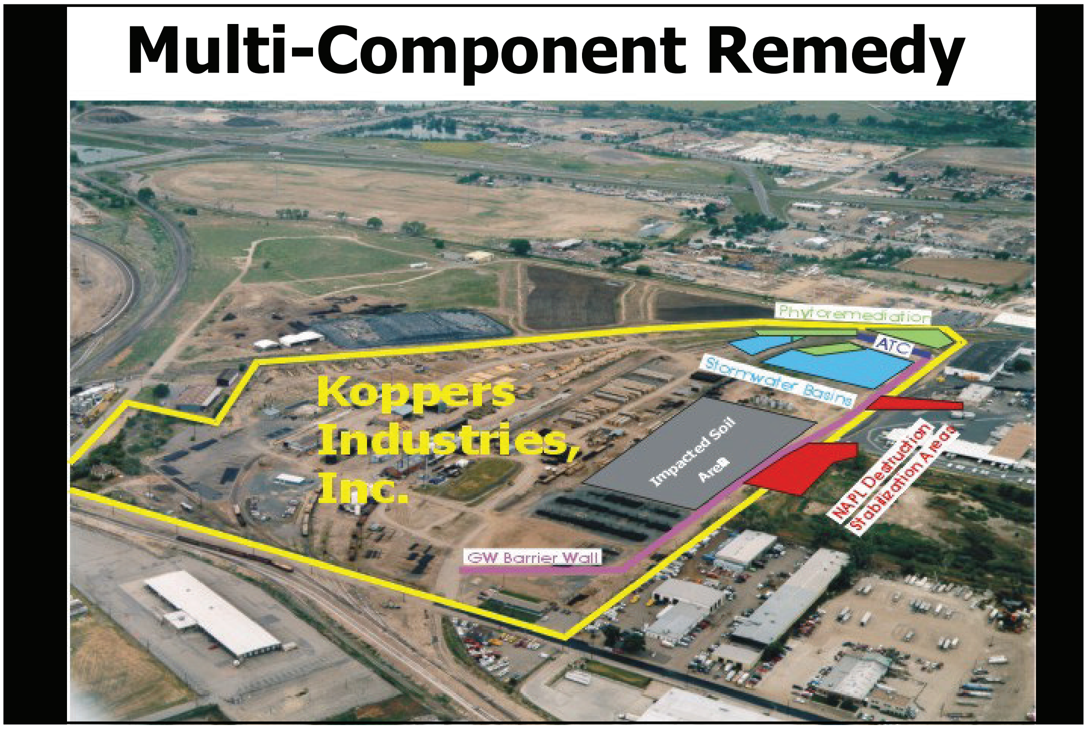
KI Denver Site

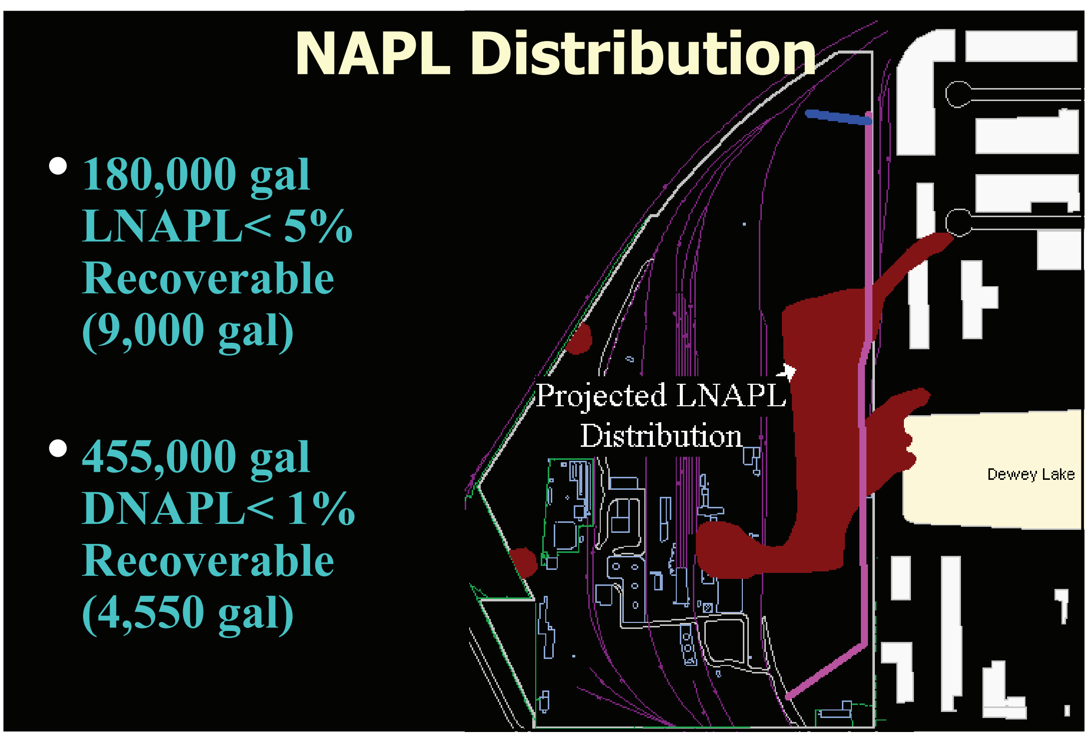
- 65-Acre Wood-Treating Site
- In operation for over 70 years
- Alluvial deposits overlying fractured low-permeability bedrock
- Creosote and pentachlorophenol NAPLs

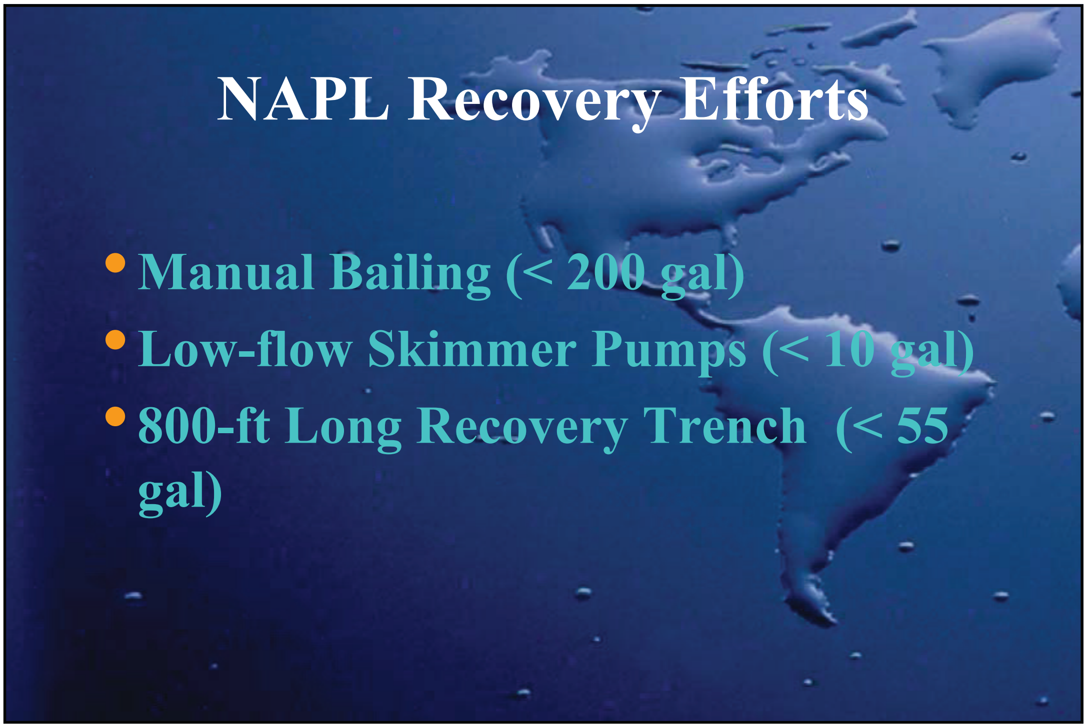
Multi-Component Remedy

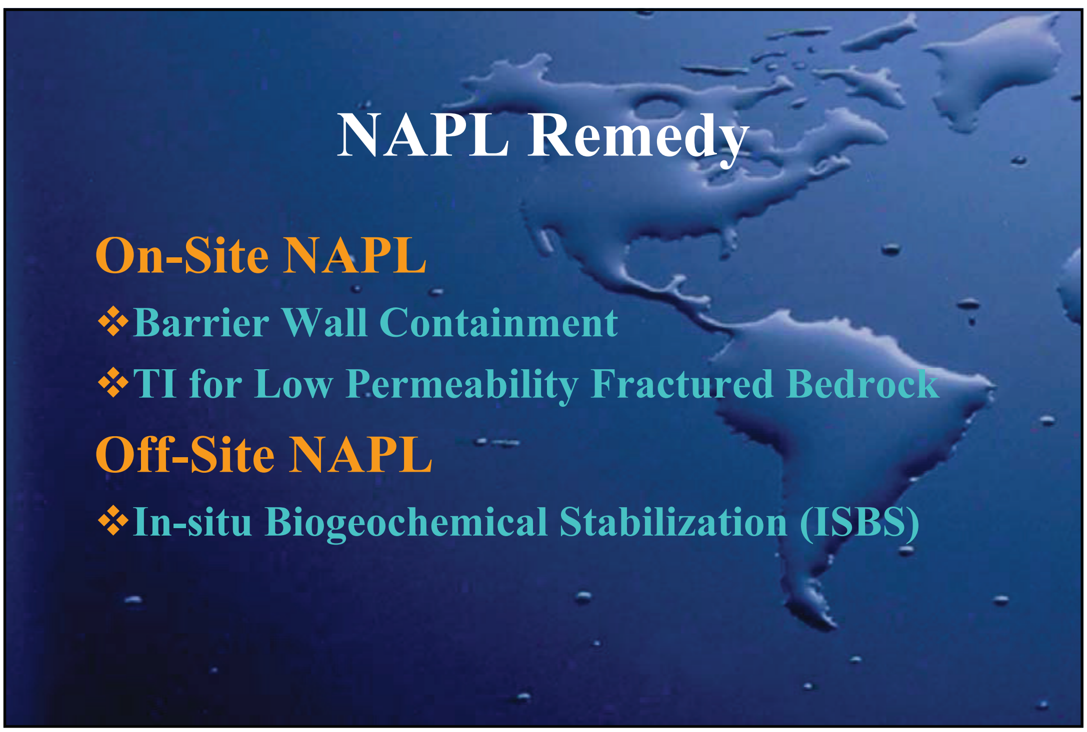
Groundwater Remedy

- Barrier Wall Containment
- In-situ Biochemical Stabilization (ISBS) NAPLs
- In-situ Aerobic Treatment Curtain (ATC)
- In-situ Anaerobic Treatment Zone (ATZ)
- Phytoremediation
- Environmental Covenant
- Monitored Natural Attenuation (MNA)


Multi-Component Remedy
Koppers Industries, Inc.
Phytoremediation
ATC
Stormwater Basins
Impacted Soil Area
NAPL Destruction/ Stabilization Areas
GW Barrier Wall


NAPL Distribution
• 180,000 gal LNAPL< 5% Recoverable (9,000 gal)
• 455,000 gal DNAPL< 1% Recoverable (4,550 gal)
Projected LNAPL Distribution
Dewey Lake


NAPL Recovery Efforts
Manual Bailing (< 200 gal)
Low-flow Skimmer Pumps (< 10 gal)
800-ft Long Recovery Trench (< 55 gal)


NAPL Remedy
On-Site NAPL
Barrier Wall Containment
TI for Low Permeability Fractured Bedrock
Off-Site NAPL
In-situ Biogeochemical Stabilization (ISBS)

ISBS Containment Remedy

Reduce the dissolution rate of organic constituents from NAPLs by:

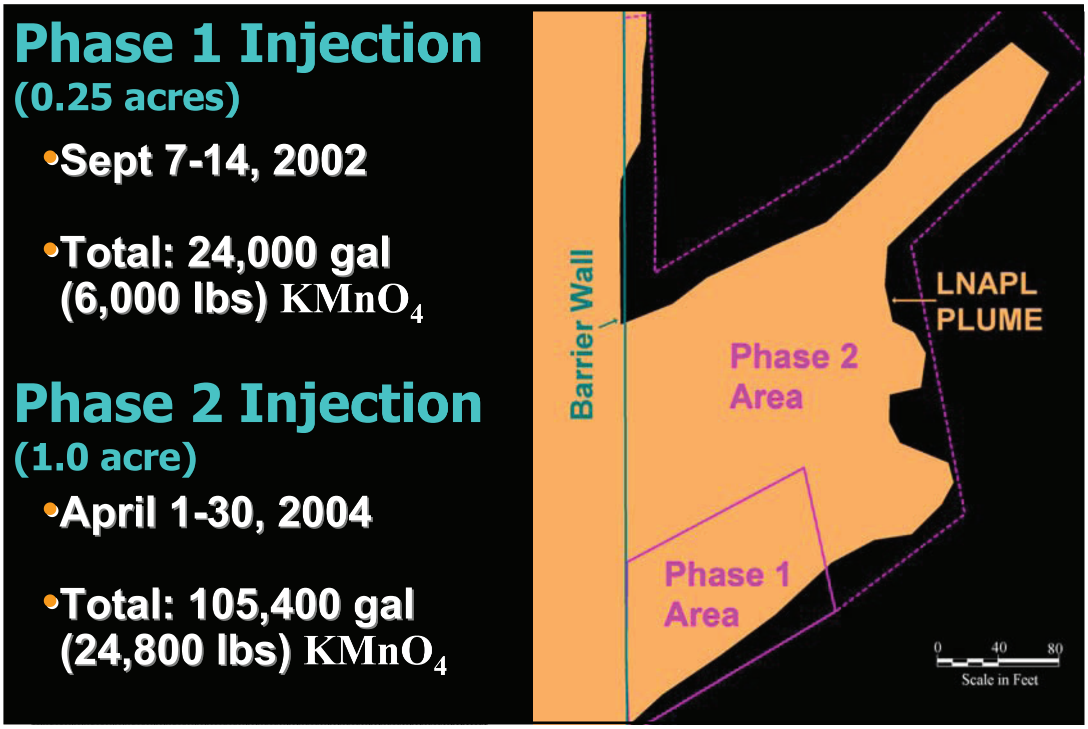
- Chemically weathering NAPLs
- Manganese dioxide coating/shell
- Reduced groundwater flux thru NAPL areas

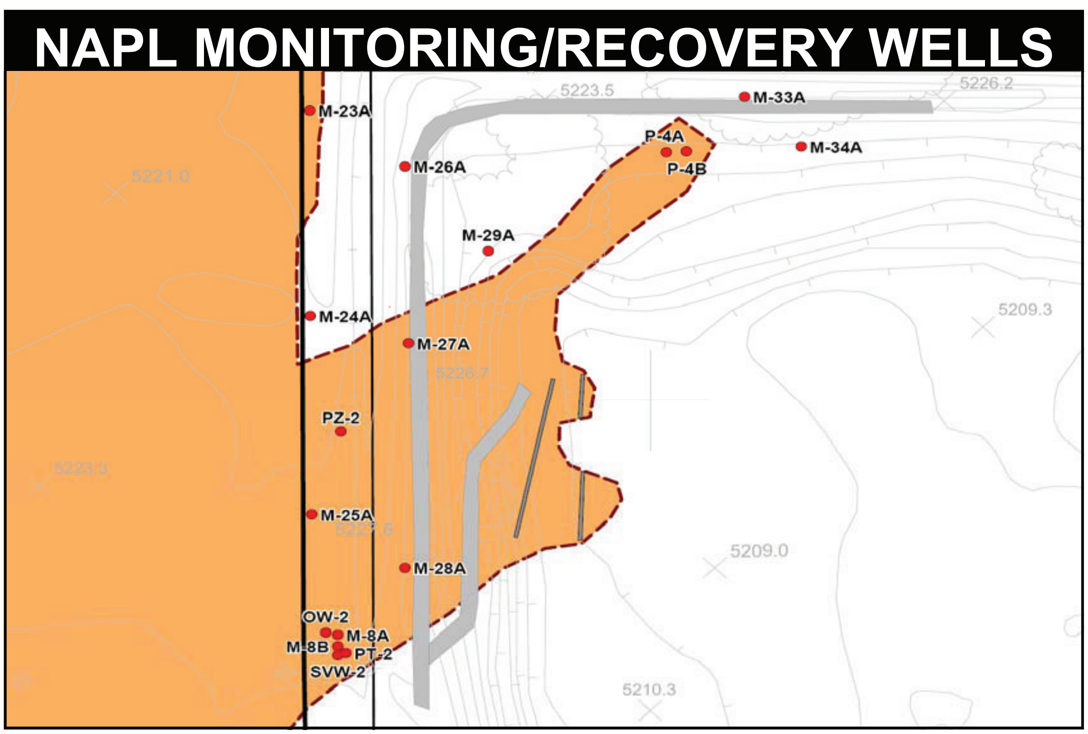
ISBS using Permanganate

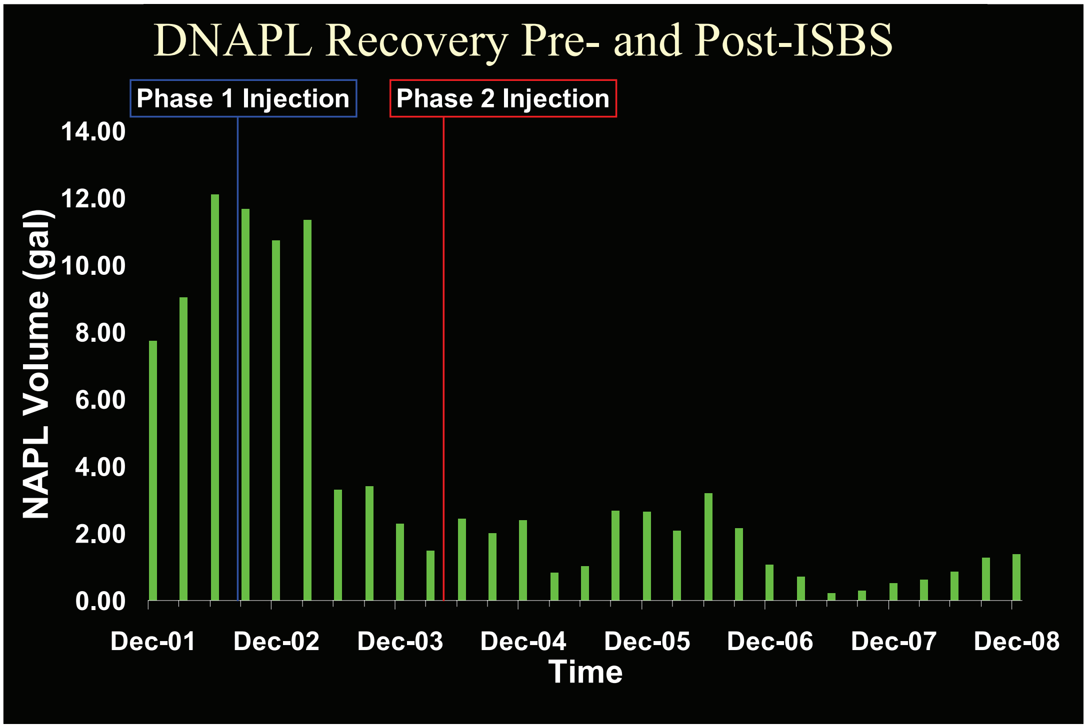
In the presence of an organic compound (R), the reactions yield either an oxidized intermediate (Rox) or CO_2, …plus MnO_2

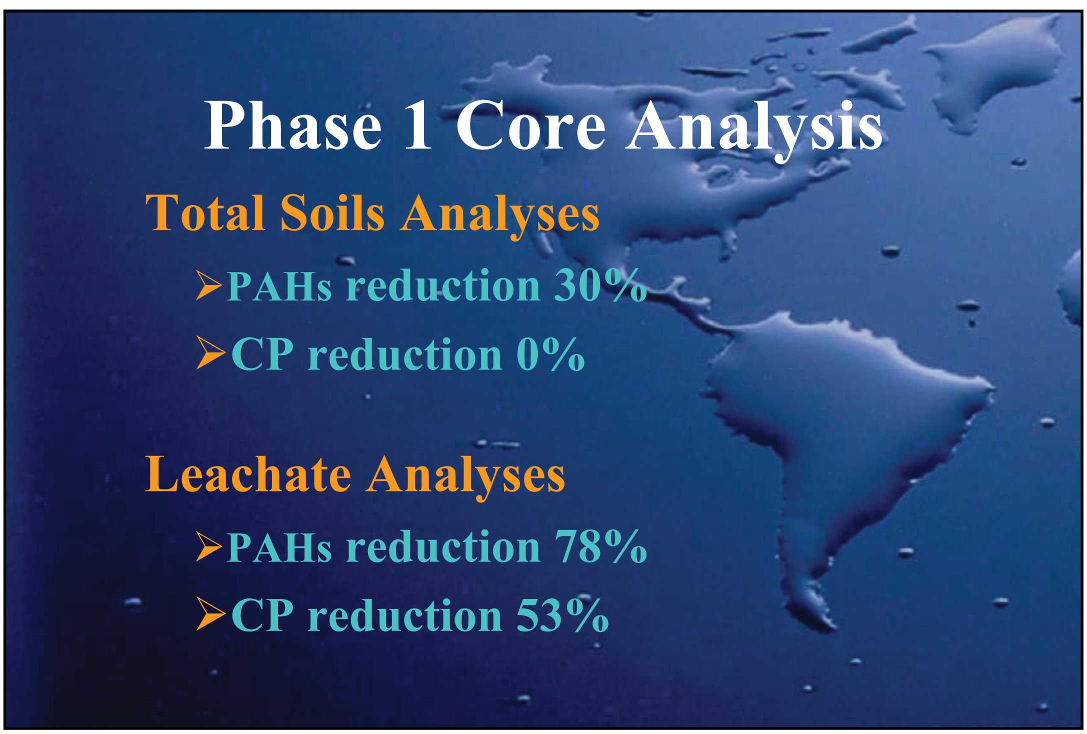
$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \text{ or } Rox$$

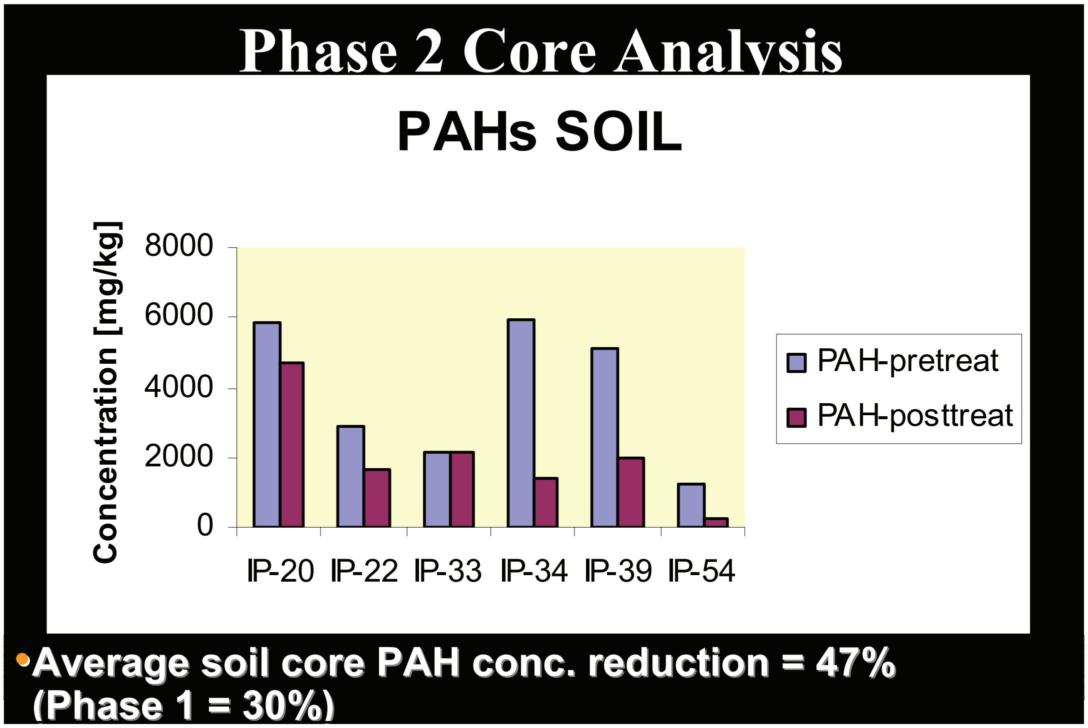
MacKinnon and Thomson (2002) J. Contam. Hydrology Vol 56 (1-2) 49-74

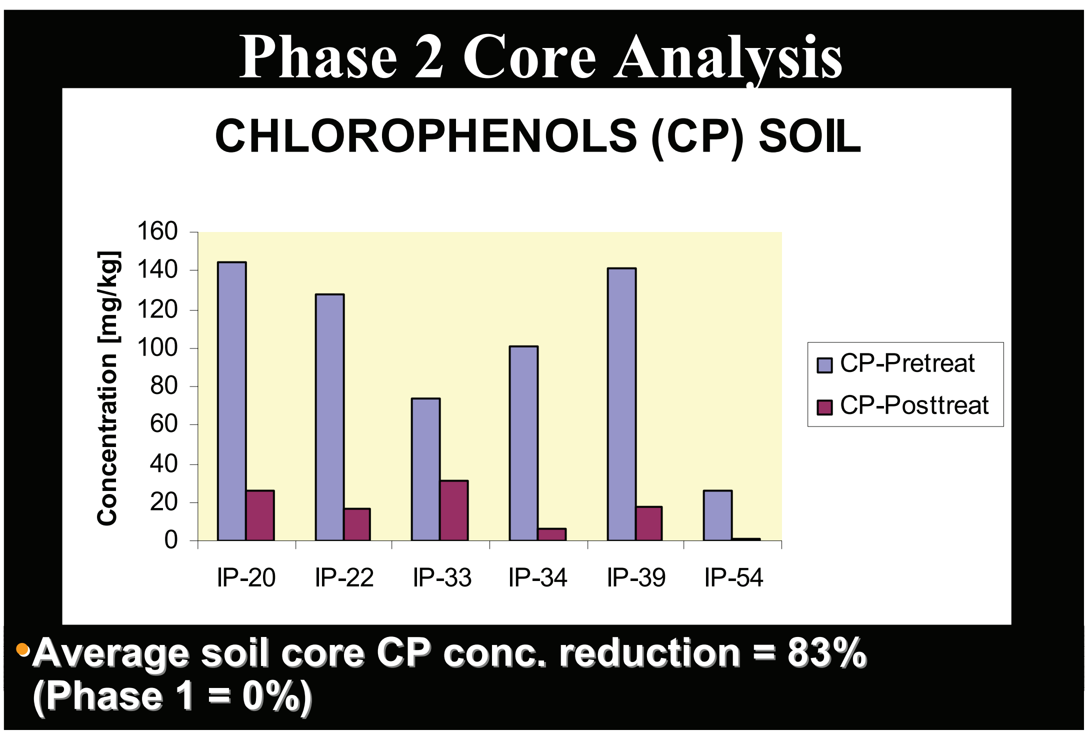

Phase 1 Injection
(0.25 acres)
•Sept 7-14, 2002
•Total: 24,000 gal (6,000 lbs) $KMnO_4$
Phase 2 Injection
(1.0 acre)
•April 1-30, 2004
•Total: 105,400 gal (24,800 lbs) $KMnO_4$
Barrier Wall
LNAPL PLUME
Phase 2 Area
Phase 1 Area
0 40 80
Scale in Feet


NAPL MONITORING/RECOVERY WELLS
M-23A
M-26A
M-33A
M-34A
P-4A
P-4B
M-29A
M-24A
M-27A
PZ-2
M-25A
M-28A
OW-2
M-8B
M-8A
PT-2
SVW-2
5223.5
5226.2
5209.3
5209.0
5210.3

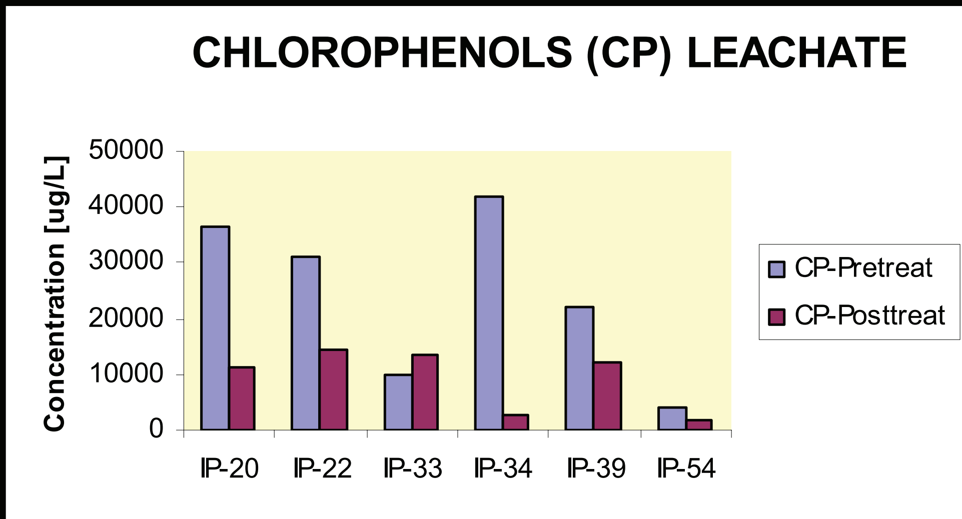

DNAPL Recovery Pre- and Post-ISBS
Phase 1 Injection
Phase 2 Injection
NAPL Volume (gal)
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
Dec-01
Dec-02
Dec-03
Dec-04
Dec-05
Dec-06
Dec-07
Dec-08
Time


Phase 1 Core Analysis
Total Soils Analyses
➢PAHs reduction 30%
➢CP reduction 0%
Leachate Analyses
➢PAHs reduction 78%
➢CP reduction 53%


Phase 2 Core Analysis
PAHs SOIL
Concentration [mg/kg]
8000
6000
4000
2000
0
IP-20 IP-22 IP-33 IP-34 IP-39 IP-54
PAH-pretreat
PAH-posttreat
•Average soil core PAH conc. reduction = 47%
(Phase 1 = 30%)

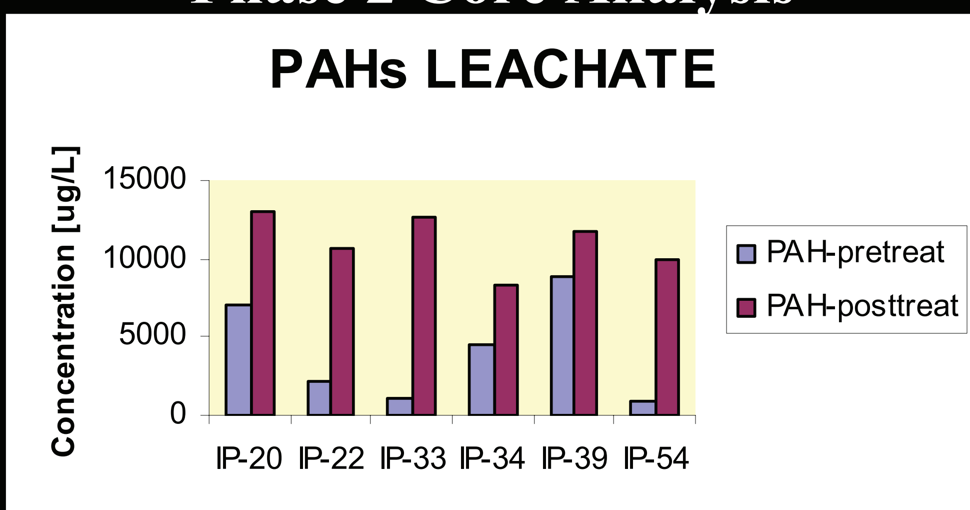

Phase 2 Core Analysis
CHLOROPHENOLS (CP) SOIL
Concentration [mg/kg]
160
140
120
100
80
60
40
20
0
IP-20 IP-22 IP-33 IP-34 IP-39 IP-54
CP-Pretreat
CP-Posttreat
•Average soil core CP conc. reduction = 83%
(Phase 1 = 0%)

Phase 2 Core Analysis



- Average leachate CP conc. reduction = 49% (Phase 1 = 53%)

Phase 2 Core Analysis



- Average leachate PAH conc. <u>increase</u> = 434% (Phase 1 = 78% reduction)

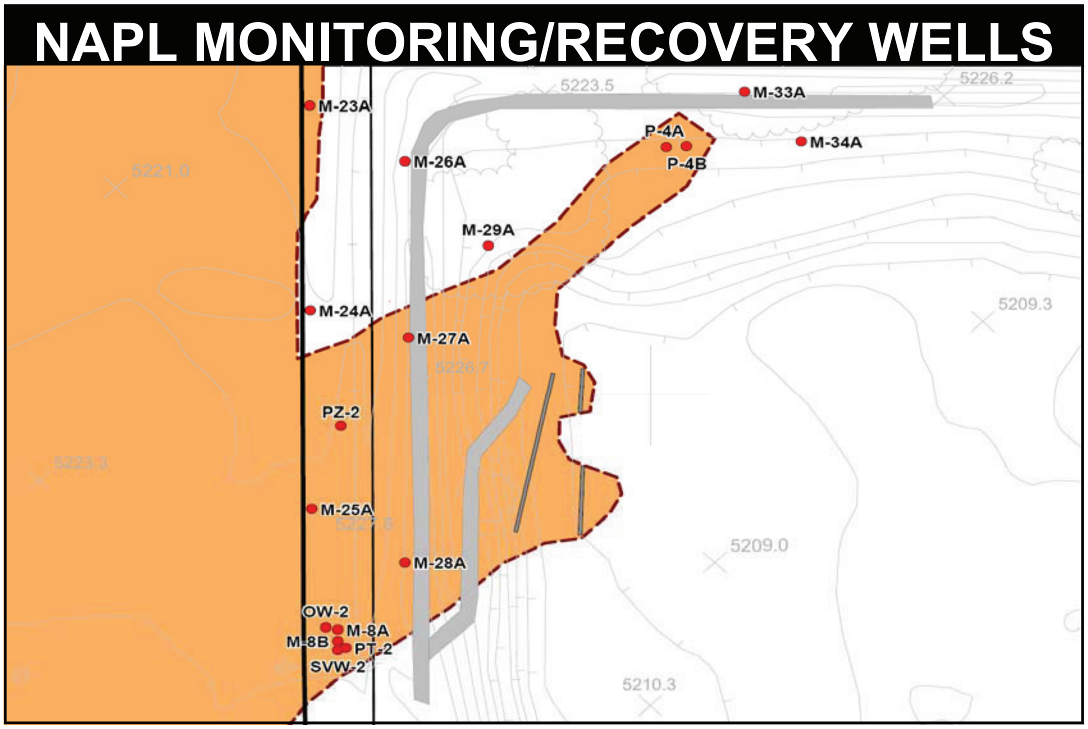
PAH Leachate Concentration Increase

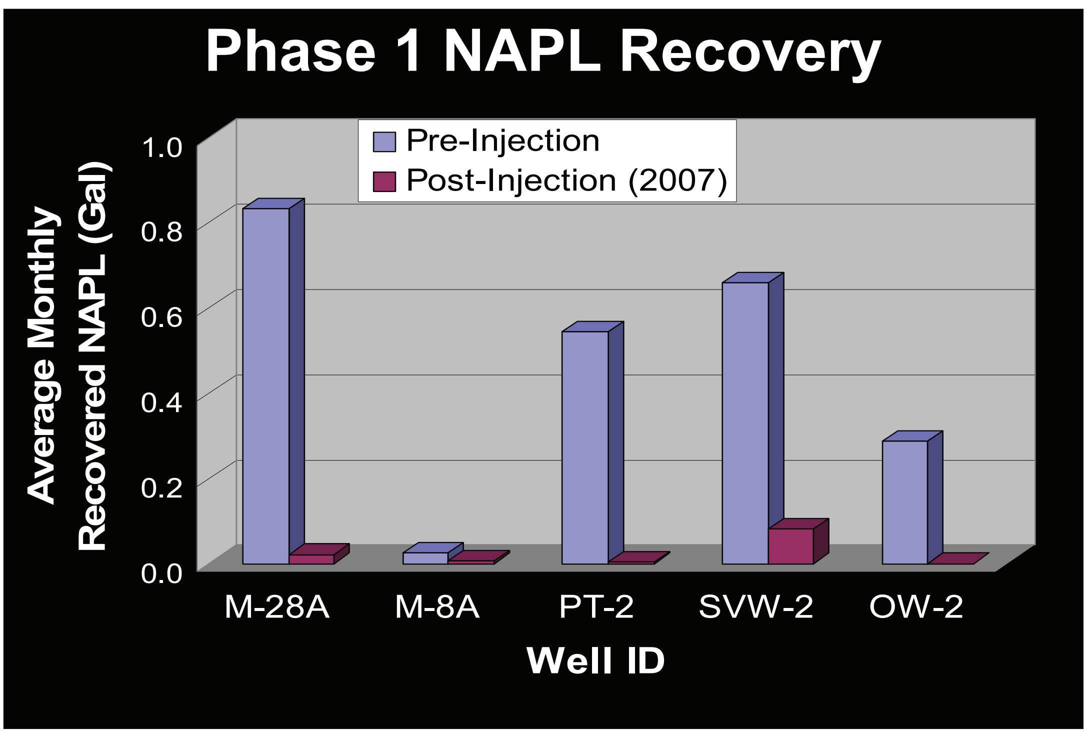
- Spatial variability: heterogeneity formation, core locations, NAPL distribution and soil sub-sampling
- $KMnO_4$ oxidation of soil humus releasing adsorbed PAHs
- K ions displacing dissolved-phase PAHs (Primarily Naphthalene) adsorbed to clay minerals

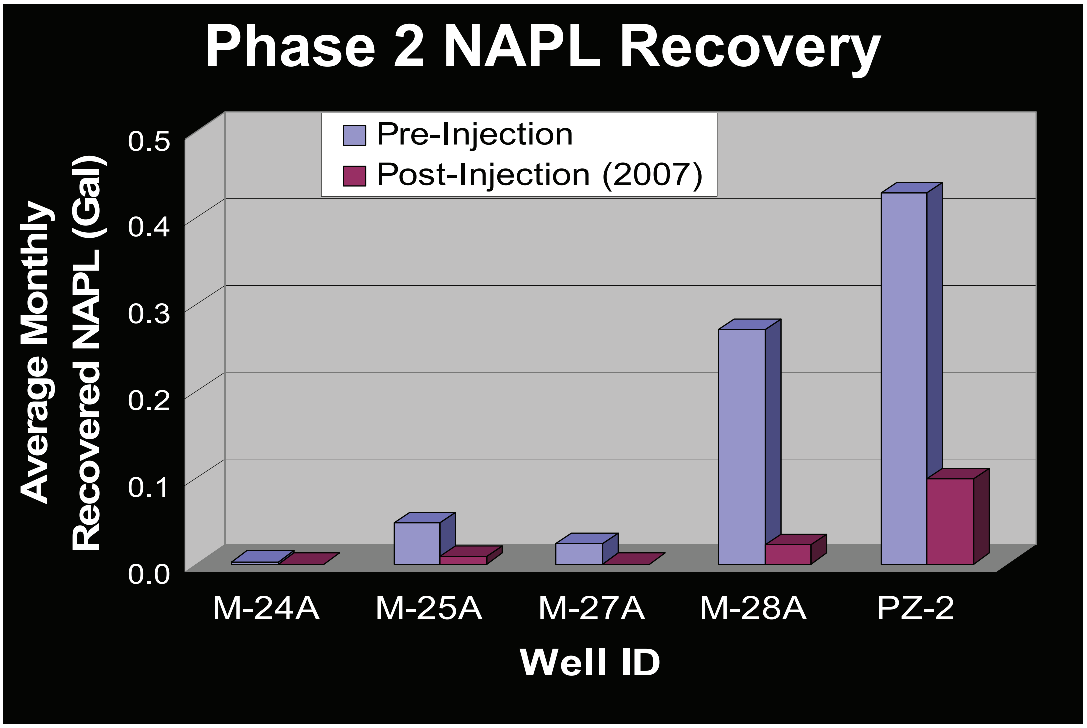
Conclusions

- Permanganate injection stabilized NAPLs and reduced GW flux
- Total PAHs and CP concentrations decreased in soil core
- Total CP concentrations decreased in leachate; total PAHs increased
- Effects on dissolved-phase GW concentrations downgradient of ISBS?? (Monitoring On-Going)


Statement of Basis (Sept 2003)
U. S. EPA Region VIII
" EPA believes that Beazer's willingness to apply innovative technologies is commendable in that it may result in superior remedies for this facility and advance the state of the science for other facilities"


NAPL MONITORING/RECOVERY WELLS
M-23A
M-26A
M-29A
M-24A
M-27A
PZ-2
M-25A
M-28A
OW-2
M-8A
M-8B
PT-2
SVW-2
M-33A
M-34A
P-4A
P-4B
5223.5
5226.2
5221.0
5209.3
5223.3
5209.0
5210.3


Phase 1 NAPL Recovery
Pre-Injection
Post-Injection (2007)
Average Monthly Recovered NAPL (Gal)
1.0
0.8
0.6
0.4
0.2
0.0
M-28A
M-8A
PT-2
SVW-2
OW-2
Well ID



Phase 2 Injection

- April 1-30, 2004
- Total: 105,400 gal of 3% (24,800 lbs) $KMnO_4$
- $KMnO_4$: 4.5 g/kg vs. 18 g/kg NOD
- Injection rate 2 to 6 gal/min