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Simultaneous Use of In Situ Chemical Oxidation (ISCO) and In Situ Solidification/Stabilization (ISS) in Remedial Applications

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Outline

- Technology overview
  - In Situ Solidification-Stabilization
  - In Situ Chemical Oxidation
- Combined Remedy
  - Synergies and Benefits
- Reagent Blend
  - Match to site specific remedial goals
- Strategies and Applications
- Case Study
- Summary

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In Situ Chemical Oxidation

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- In situ chemical oxidation (ISCO)
  - Powerful ***destructive*** remedial technology
  - Applied via injection, recirculation, backfill amendment, and soil mixing

ISCO works by establishing contact between a sufficient mass of activated persulfate and the mass of contaminant

- Alkaline activated persulfate
  - Thousands of successful applications
  - Oxidative and reductive destructive pathways
    - Complex comingled plumes
  - Minimized corrosivity on carbon steel equipment
  - Little to no heat or gas evolution

In Situ Solidification-Stabilization

In Situ Solidification-Stabilization (ISS)

- Contaminant ***immobilization or mass flux reduction***
- Decreases the hydraulic conductivity of soils
- Compressive soil strength influenced by type and dose of reagents
- Applied via soil mixing/blending

ISS is commonly used to immobilize highly contaminated petroleum hydrocarbon sites (MGP sites, etc)

Combining ISS and ISCO

- ISCO and ISS are already being combined at several sites
  - Example: 2008 Turtle Bayou (URS-AECOM)
    - COCs: BTEX, cVOCs and PAHs
    - Klozur SP, hydrated lime, and Portland cement
      - 760,000 lbs Klozur SP
    - Met remedial goals
      - ISCO: 84% to 97% treatment
      - ISS: Stabilized soils

Wiley and Block, (2010) D-021, "Chemical Oxidation Using Sodium Persulfate at a Superfund Site in Texas," Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA

Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

- Highly contaminated soils
  - >36,900 mg/Kg TPH
  - ~6,800 mg/Kg BTEX
  - ~13,400 mg/Kg Naphthalene (Nap)
  - ~16,900 mg/Kg 17 PAHs (not including Nap)
- Klozur SP: Portland Cement (PC) ratio (1:2 w/w)
  - **CaO in PC facilitates persulfate activation**
- ISCO:
  - Persulfate underdosed for complete treatment of TPH
  - Preferential treatment of soluble contaminants

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Where to Use ISS and ISCO

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- Source zones
  - Very highly contaminated sites (NAPL)
    - Petroleum hydrocarbon (MGP, etc)
    - cVOC
- To create hydraulic barriers
  - Lower hydraulic conductivities observed in ISS with ISCO rather than ISS alone
- Soil mixing application strategy
- Different ratio of reagents to accomplish site specific goals
  - Balance contaminant destruction, solidification, and post application site soil characteristics

Synergies of ISCO and ISS

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Combining ISCO and ISS can make each technology better

ISCO benefits:

1. Alkalinity from ISS reagents can be used to activate Klozur SP
2. Post ISCO soil mixing application soils can have their geotechnical characteristics enhanced with low amounts of ISS reagents

ISS benefits:

3. Contaminant destruction by ISCO can enhance stabilization from ISS
   - Helps the cementitious process
   - Less contaminant to immobilize = lower leachate concentrations
4. Less overall mass of reagents results in less displaced soil
5. Better ability to balance achieving both hydraulic conductivity and compressive soil strength

6. Contaminant destruction and immobilization in single soil mixing application (combined remedy)
   - Saving project time and overall cost

ISCO Benefits: Alkalinity

ISS reagents

- Portland cement (~65% CaO)
- Calcium hydroxide [$Ca(OH)_2$]
- Calcium oxide (CaO)
- Fly Ash (Class C & F)
- Blast furnace slag
- Lime kiln dust
- Cement kiln dust
- Pozzolans
- Bentonite

Common ISS reagents can activate Klozur SP

Activated Klozur persulfate reagents

- Klozur SP (oxidant)
- Alkaline activation*. One (or more) of the following:
  - 25% NaOH (typical for injections)
  - Calcium hydroxide [$Ca(OH)_2$]
  - Calcium oxide (CaO)
- Heat activation
  - CaO upon hydration releases heat

* PeroxyChem LLC ("PeroxyChem") is the owner of U.S. Patents No: 7,576,254 and its foreign equivalents. The purchase of PeroxyChem's Klozur® persulfate includes with it, the grant of a limited license under the foregoing patent at no additional cost to the buyer.

ISCO Benefits: Soil Strength

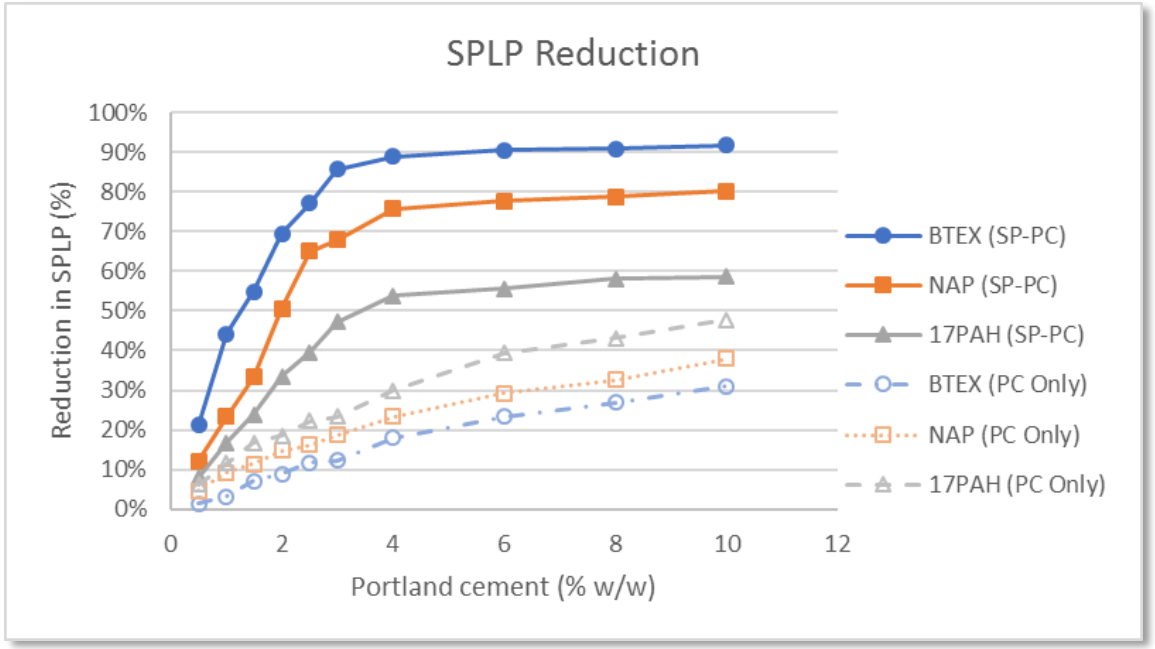
- ISCO applied with soil mixing and no ISS reagents may not have desirable post application soil characteristics
  - Low levels of ISS reagents can enhanced post application soil characteristics
    - Site specific (approximately 0.5 to 1.5% Portland cement)

General Relationship between Soil Consistency and Unconfined Compressive Strength				
Consistency	Unconfined Compressive Strength (UCS) Ranges			
	psi		kPa (KN/m^2)	
	Low	High	Low	High
Very soft	0	3	0	24
Soft	3	7	24	48
Medium	7	14	48	96
Stiff	14	28	96	192
Very Stiff	28	56	192	383
Hard	>56		>383	

Typical target range for “workable” soils
20-50 psi

ISS Benefits: Leachate Concentrations

- Contaminant leachate reduction
  - Greater reduction in leachate concentrations with Klozur SP and Portland cement than Portland cement only
  - ISCO preferentially reduced more soluble contaminants
  - Portland cement alone only preferentially reduced leachate concentrations of larger, less soluble compounds



SPLP (synthetic precipitation leaching procedure)

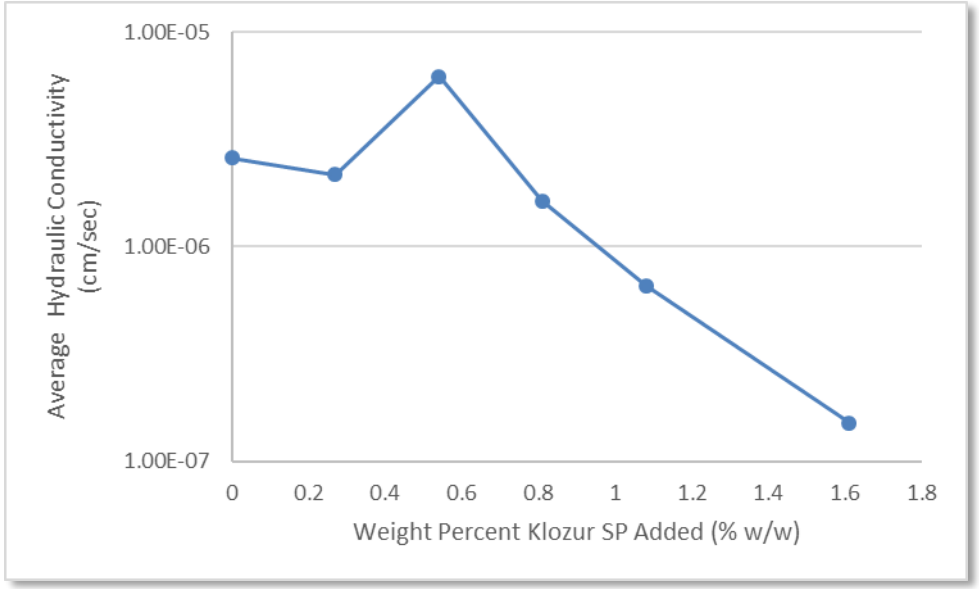
Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

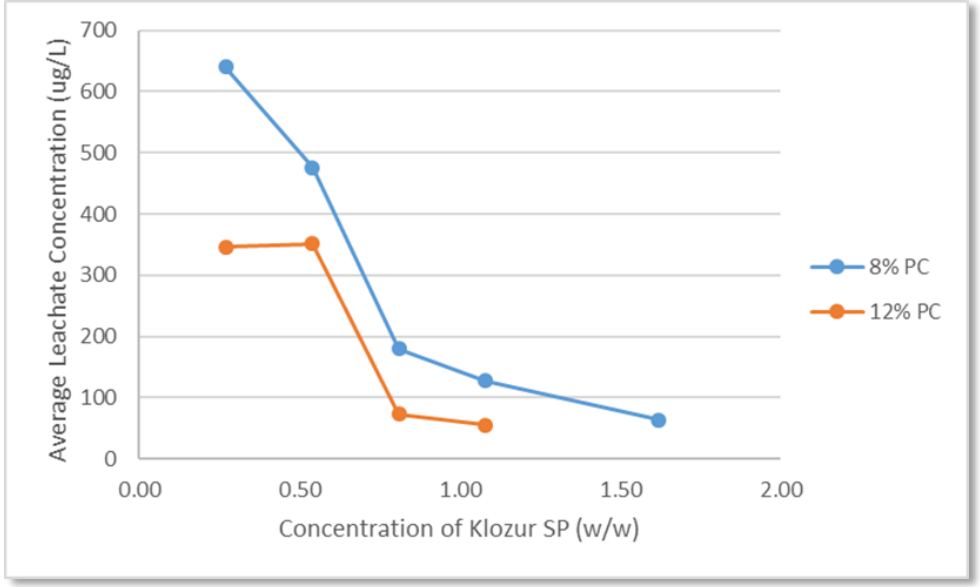
ISS Benefits: Enhanced Cementitious Process

- Organic contaminants can interfere with cementitious process
  - Soils covered in oil do not bind well
- Sufficiently dosed ISCO oxidizes the organics, enhances the cementitious process

Highly contaminated soils:
- Hydraulic conductivity and compressive soil strength a function of Portland cement (PC)

Less contaminated soils:
- Hydraulic conductivity a function of Klozur SP and PC





Courtesy of Brasfond

ISCO-ISS: Combined Remedy

Combined remedy in a single soil mixing application

1. Reduce contaminant mass with ISCO
2. Stabilize/solidify the remaining contaminant mass with ISS
3. Optimize post application soil characteristics

Ratio of Reagents

- ISCO and ISS reagents can be combined for their mutual benefit
- The ratio of reagents can adjusted to achieve site specific remedial goals

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ISS-ISCO Reagent Ranges

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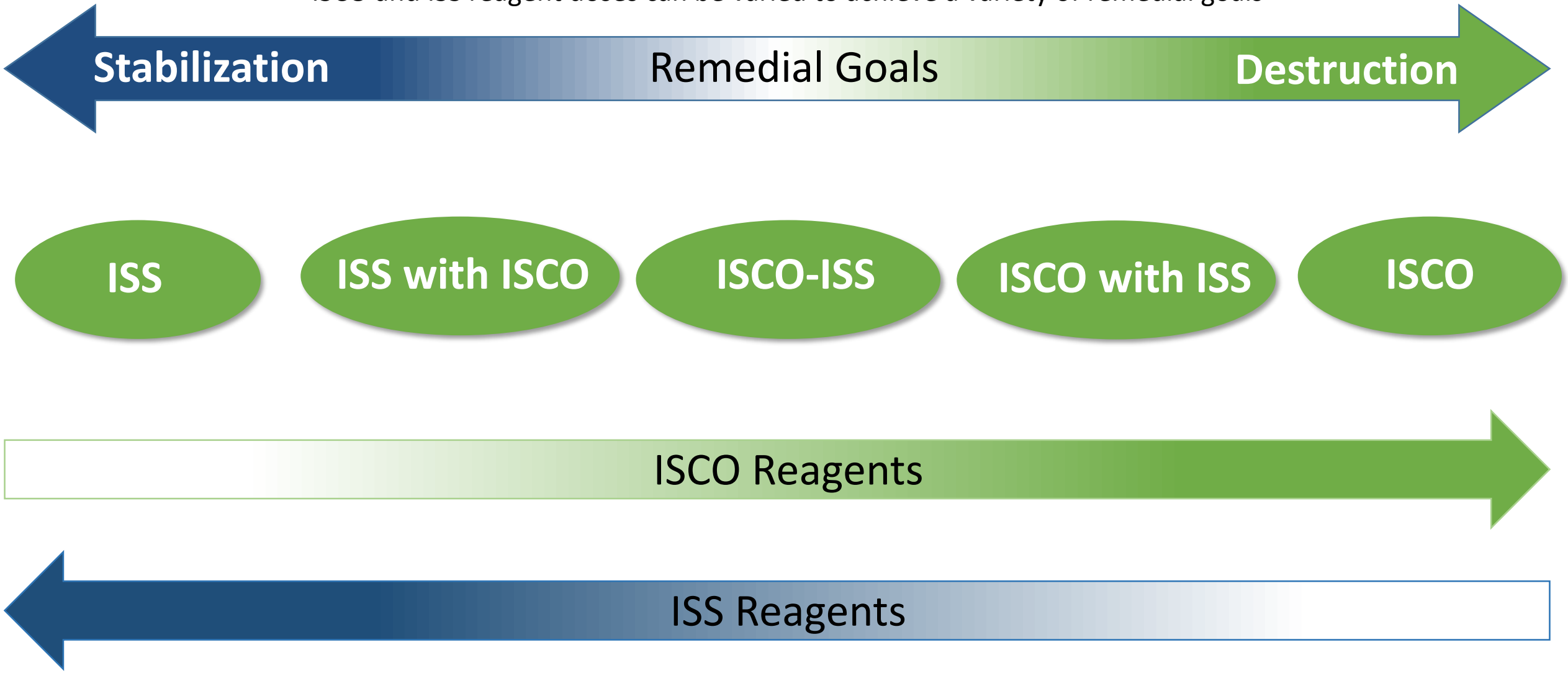
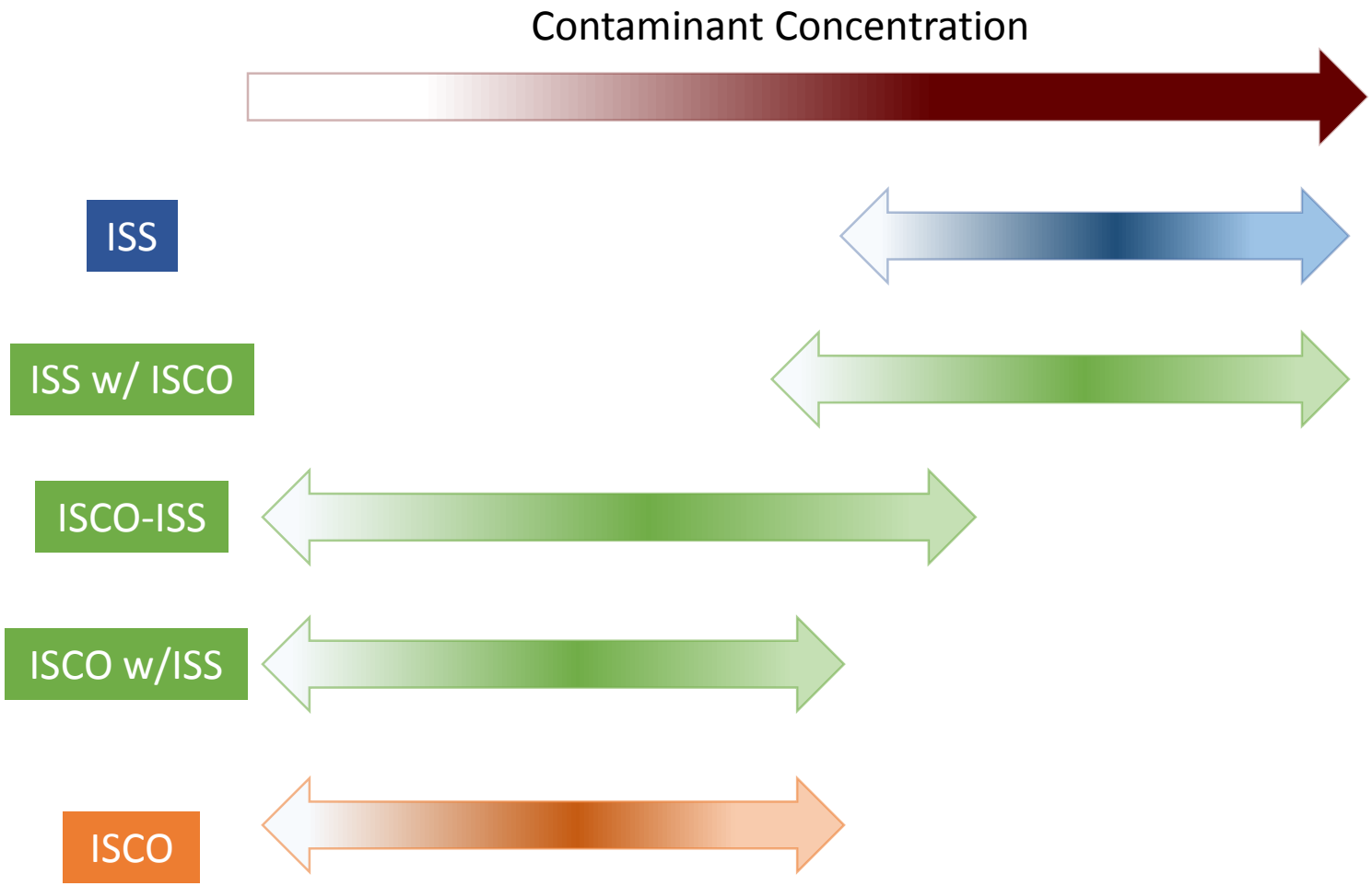
ISCO and ISS reagent doses can be varied to achieve a variety of remedial goals



Contaminant Concentration

General Strategy based on contaminant concentration

- Highest concentrations increasingly favor stabilization (i.e. >5,000 mg/Kg)
- Moderate-High concentrations favor ISCO or combined remedy (i.e. 1,000 to 10,000 mg/Kg)
- Lower concentrations increasing favor ISCO or combined remedy (i.e. <1,000 mg/Kg)



Stabilization vs Destruction

1. ISS (with ISCO)

- Remedial Goal:
  - Immobilize contaminants
  - Post application soil characteristics
- Add Klozur SP:
  - Reduce soil displaced
  - Better influence over:
    - Hydraulic conductivity
    - Compressive soil strength
  - Lower leachate concentrations

3. ISCO-ISS

- Remedial Goals:
  - Single application
    - Contaminant Mass Reduction
    - Immobilize residual contamination
    - Target post application soil characteristics
- Adjust reagent blends to target site specific remedial goals

2. ISCO (with ISS)

- Remedial Goal:
  - Contaminant Mass Reduction
- Add ISS reagents:
  - Target post application site geotechnical characteristics
    - Compressive soils strength
  - Soil mixing applications (if needed)

Can be a lower cost alternative to:

- ISS alone, sheet piling or excavation
- Combined remedy in single application

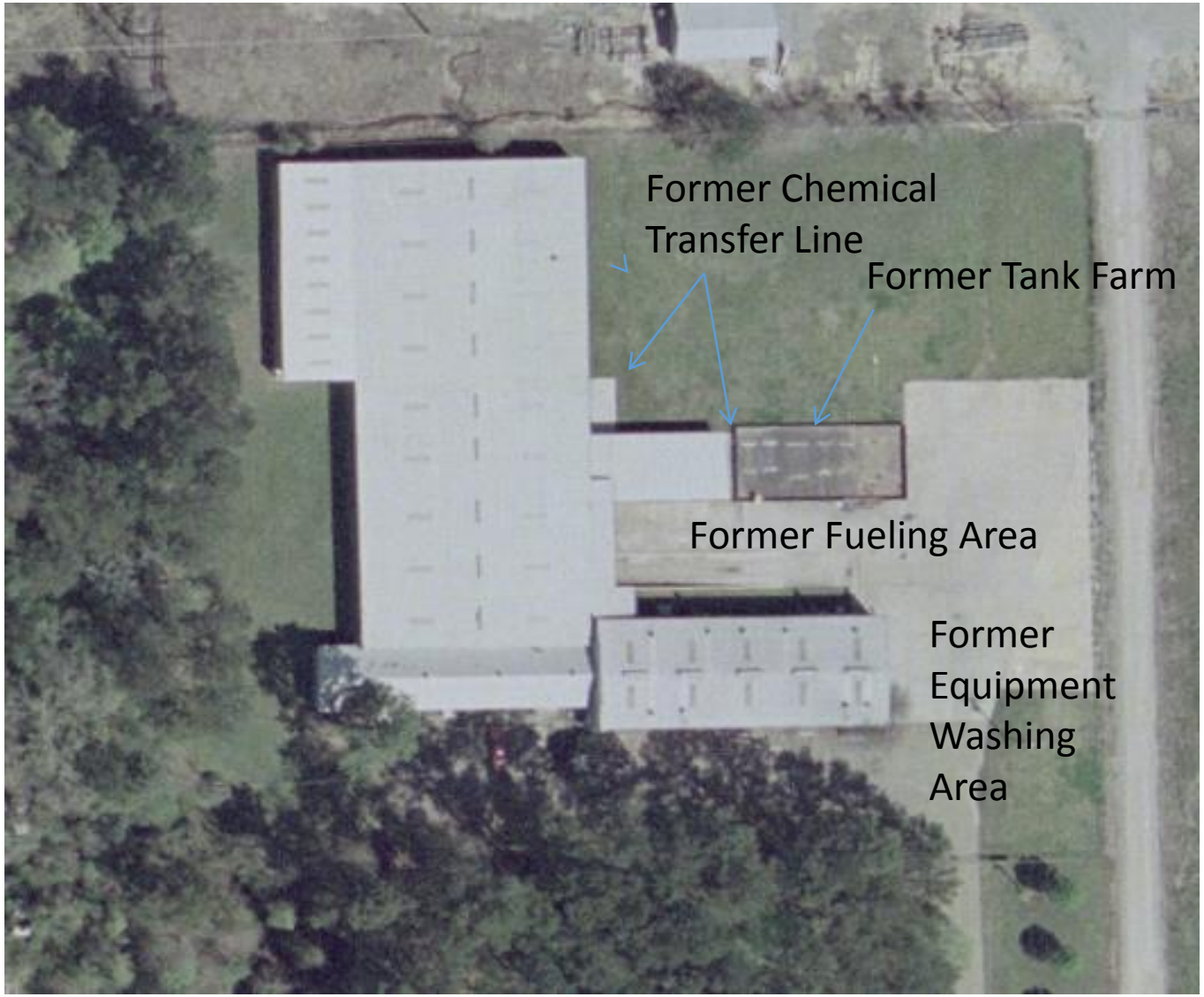
Case Study

- Industrial Facility in Baton Rouge.
- Pilot test and subsequent full scale initiated in 2006.
- Historical facility activities indicated potential presence of chlorinated solvent and petroleum mass.
- Elevated levels of chlorinated and petroleum related COCs associated with past facility operations present in soil and shallow ground water.

Project Challenges

- Affected shallow soil and perched water acting as a continuing source;
- Heterogeneous shallow lithology;
- Property had been sold and new property owners wished to replace storage/parking facilities following any pavement removal required for remediation.

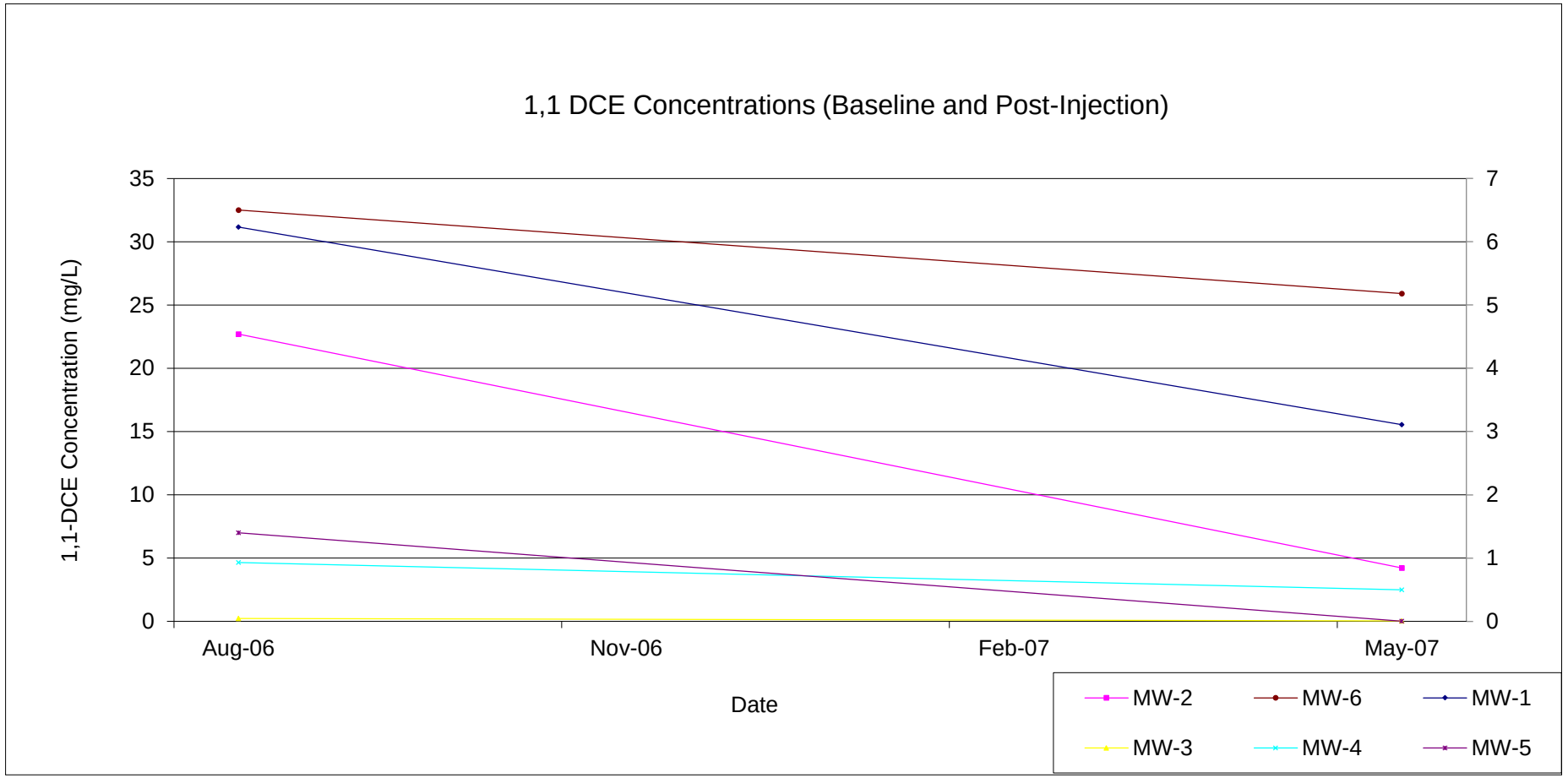
Source Areas Discovered at Inactive Facility



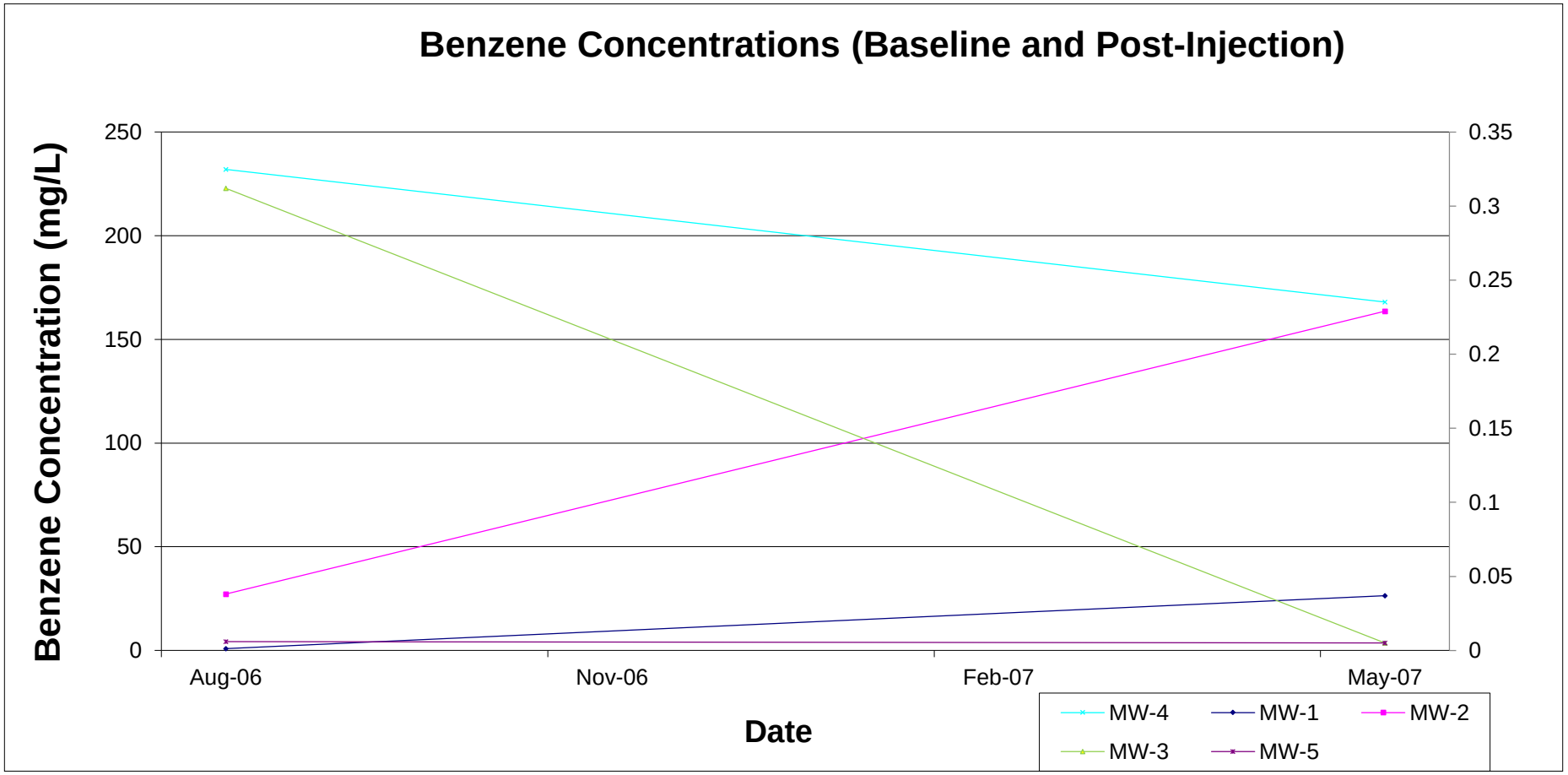
Persulfate Injection Pilot Study

- Injection pilot test conducted in 2006 using activated persulfate;
- Targeted dissolved mass of DCE and Benzene
- A total of approximately 14,000 lbs sodium persulfate and 1,600 gallons of sodium hydroxide were injected at depths of 13 to 27 feet bgs;
- Shallow ground water monitoring indicated injection efficacy;
- Preferential pathways/surface expression may have limited oxidant contact with the contaminated soil at shallower depths.
- Long-term monitoring did not indicate dissolved mass rebound.

Persulfate Injection Pilot Study



Persulfate Injection Pilot Study



Full Scale Treatment Design And Implementation

- Contamination identified south of the former Tank Farm (in a former fueling area), in the vicinity of a former chemical transfer line that ran from the Tank Farm to the main building, and on the east side of the site where equipment was historically washed;
- Former Tank Farm, chemical line, and concrete over former fueling area were removed prior to mobilization.
- Geoprobe sampling conducted throughout the area to determine treatment locations

General Process

✓Treatment areas subdivided into ten treatment cells measuring approximately between 300 and 400 ft2 in areal extent.

✓Approximately 10 -20 pounds (lbs) per ft^3 of dry, Klozure® brand sodium persulfate and approximately 2% to 3% Quicklime by volume were blended with soils in each cell to the total treatment depth (i.e., 20 ft bgs) using the Redox Tech, LLC blending equipment.

✓Each cell was blended in two 10-ft lifts, 0-10 ft bgs and 10-20 ft bgs. Higher levels of Quicklime (3% by volume) used for the upper 10 foot lifts for stabilization.

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Blending Cells

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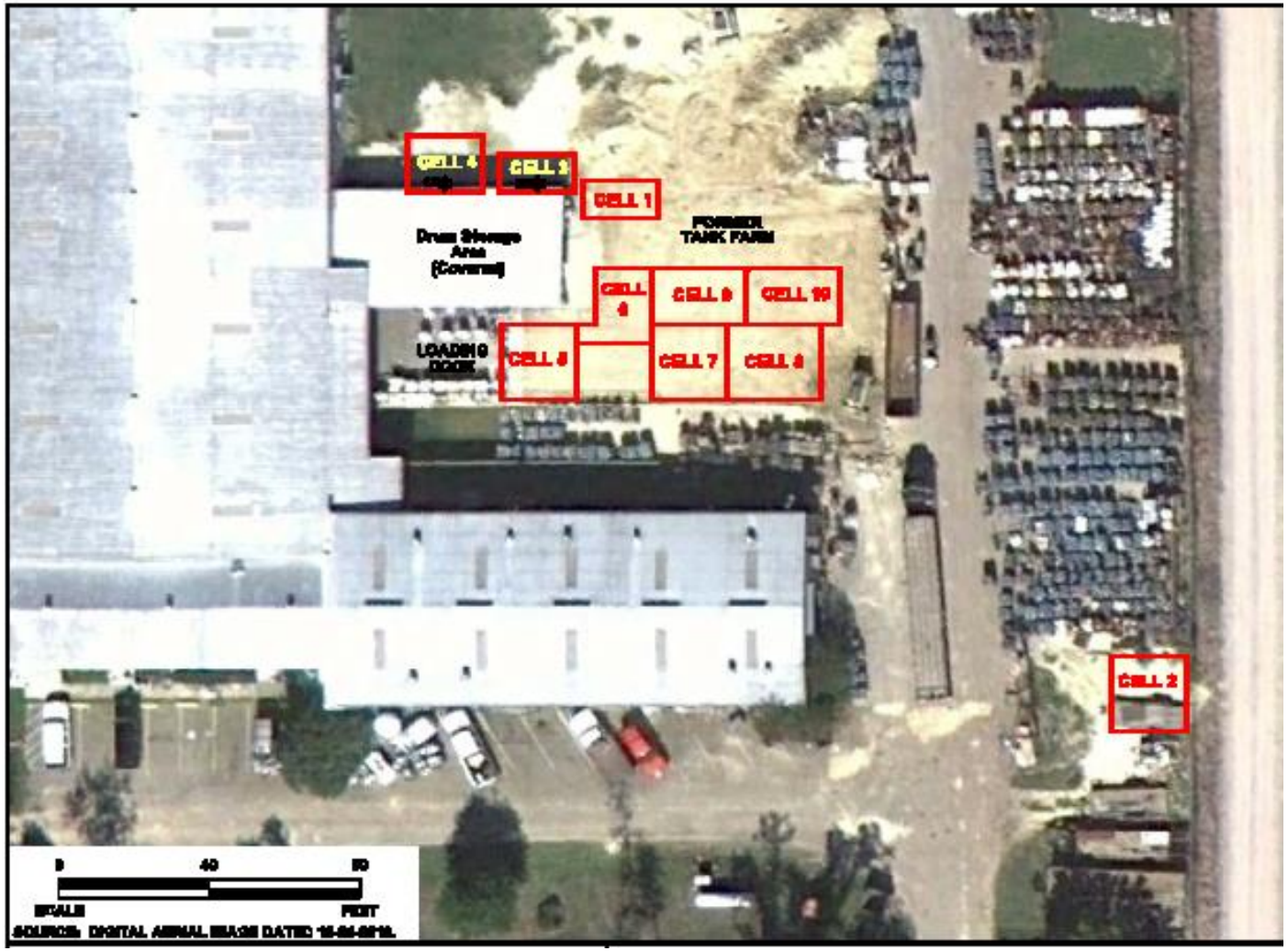

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Klozur Application

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Application & Soil Blending

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In-Situ Soil Blending

- Destroy COCs in soil and shallow ground water by increasing contact between the contaminants and oxidant;
- Reduce the costs associated with the generation and disposal of potentially hazardous waste by conducting remediation in-situ;
- Ensure the soil is stable following the blending activities so that parking/storage facilities could be re-constructed over the treatment area in a reasonable amount of time;
- Soil blending contractor was chosen after cost/benefit analysis of available blending methods (e.g., augers, excavators).

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Treated Soil

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Blending operations resulted in the management of “fluffed” soil

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Site Restoration

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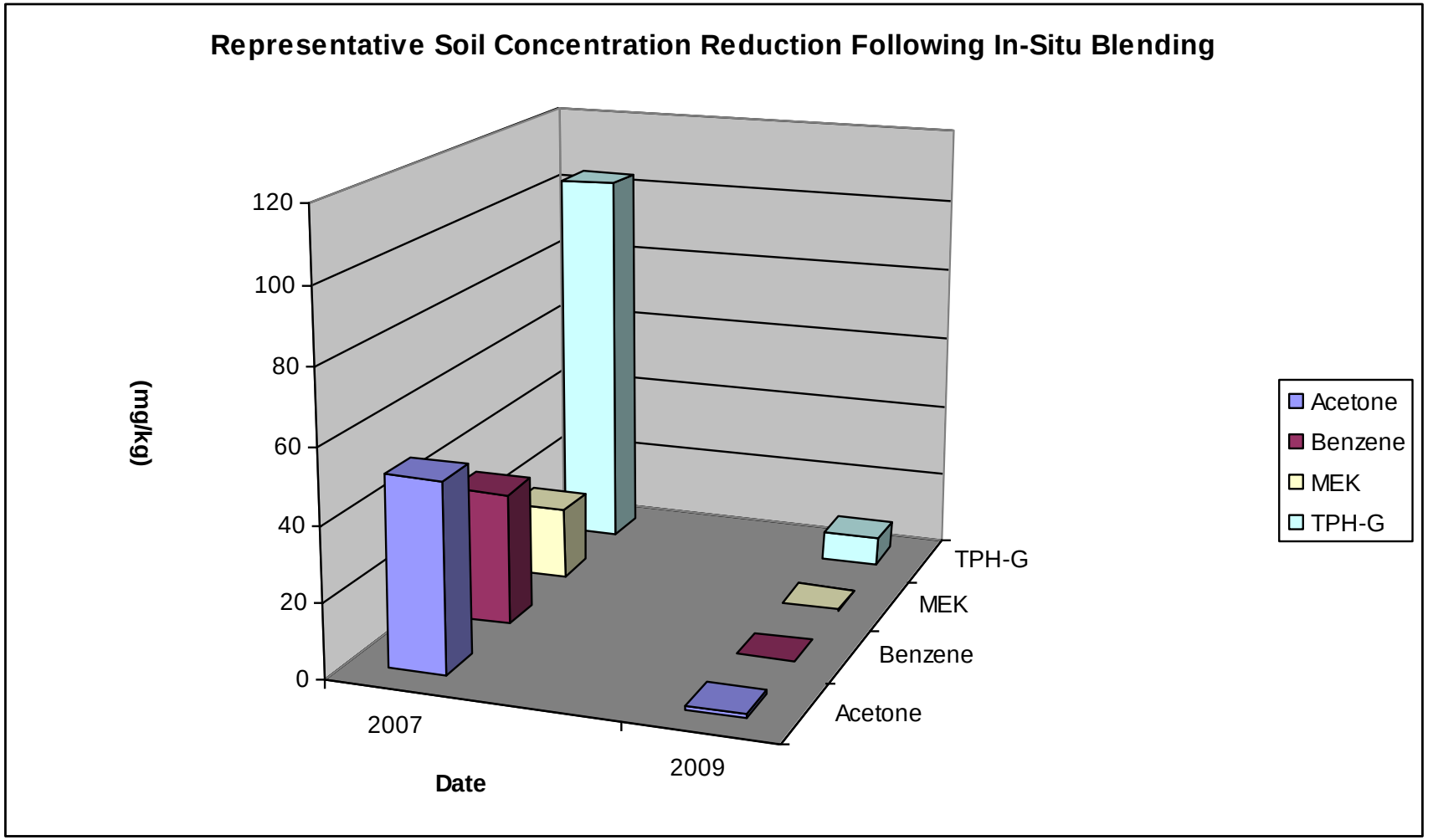
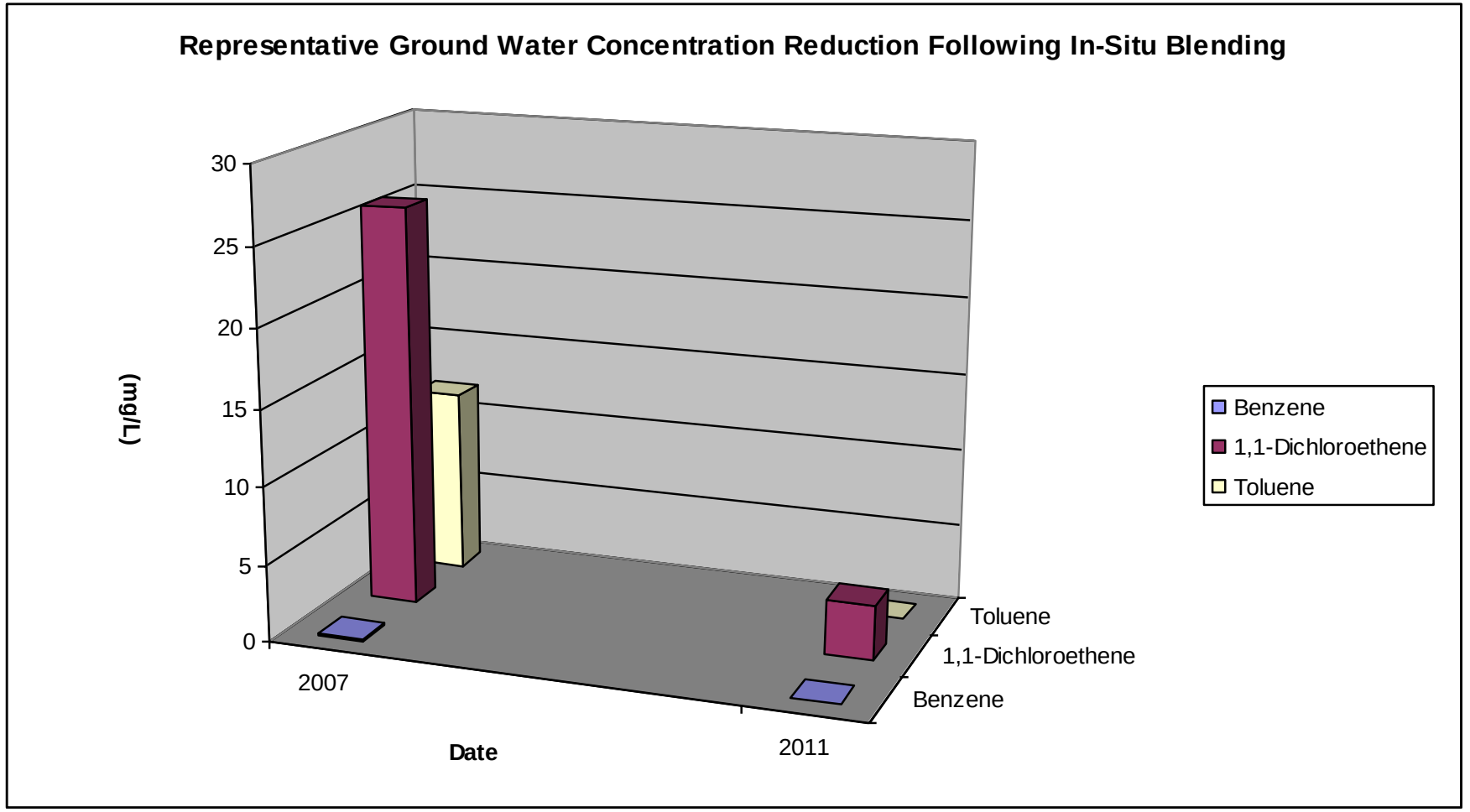
Site Restoration

Soil Treatment Results



Groundwater Treatment Results



Results and Observations

- COCs in soil and ground water showed orders of magnitude reductions;
- Use of the large quantities of calcium carbonate resulted in the management of low pH water;
- Large quantities of “fluffed” blended soil (approximately 15-20% by volume) were generated. The “fluffed” soil was approved for onsite reuse by the regulatory agency;
- Removal of VOCs was facilitated by the high temperatures resulting from the hydration of calcium oxide;
- Geotechnical testing determined that the soil conditions in the treated area were suitable for slab-on grade construction assuming proper preparation;
- Special drilling equipment (i.e. sonic) was required to install monitoring wells in the treated areas because conventional augers could not penetrate the treated soil.

Post-Remediation and Reconstruction

Summary

- Blends of ISCO and ISS using soil mixing can be a powerful combined remedy
  - Degrades the contaminant
  - Reduces contaminant flux
  - Controls post-application geotechnical characteristics of a site
- Has been found to be lower cost alternative
  - Less soil displaced, less mixing/handling
  - Combined remedy in a single application
- Technology synergies:
  1. Shared alkaline sources
  2. Contaminant degradation by ISCO can reduce leachate (SPLP) concentrations
  3. ISCO can oxidize organics interfering with the cementitious process resulting in lower hydraulic conductivities if dosed appropriately
  4. Control over post soil mixing application soil characteristics

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Questions

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