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# Monitoring Programs for Klozur® Persulfate Applications: Information Needed Before, During and After an Application

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# Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**

1. Klozur® persulfate
2. Klozur® CR

***In Situ Chemical Reduction***

3. EHC® Reagent
4. EHC® Liquid
5. Daramend® Reagent

***Aerobic Bioremediation***

6. Terramend® Reagent
7. PermeOx® Ultra

***Immobilization/Stabilization***

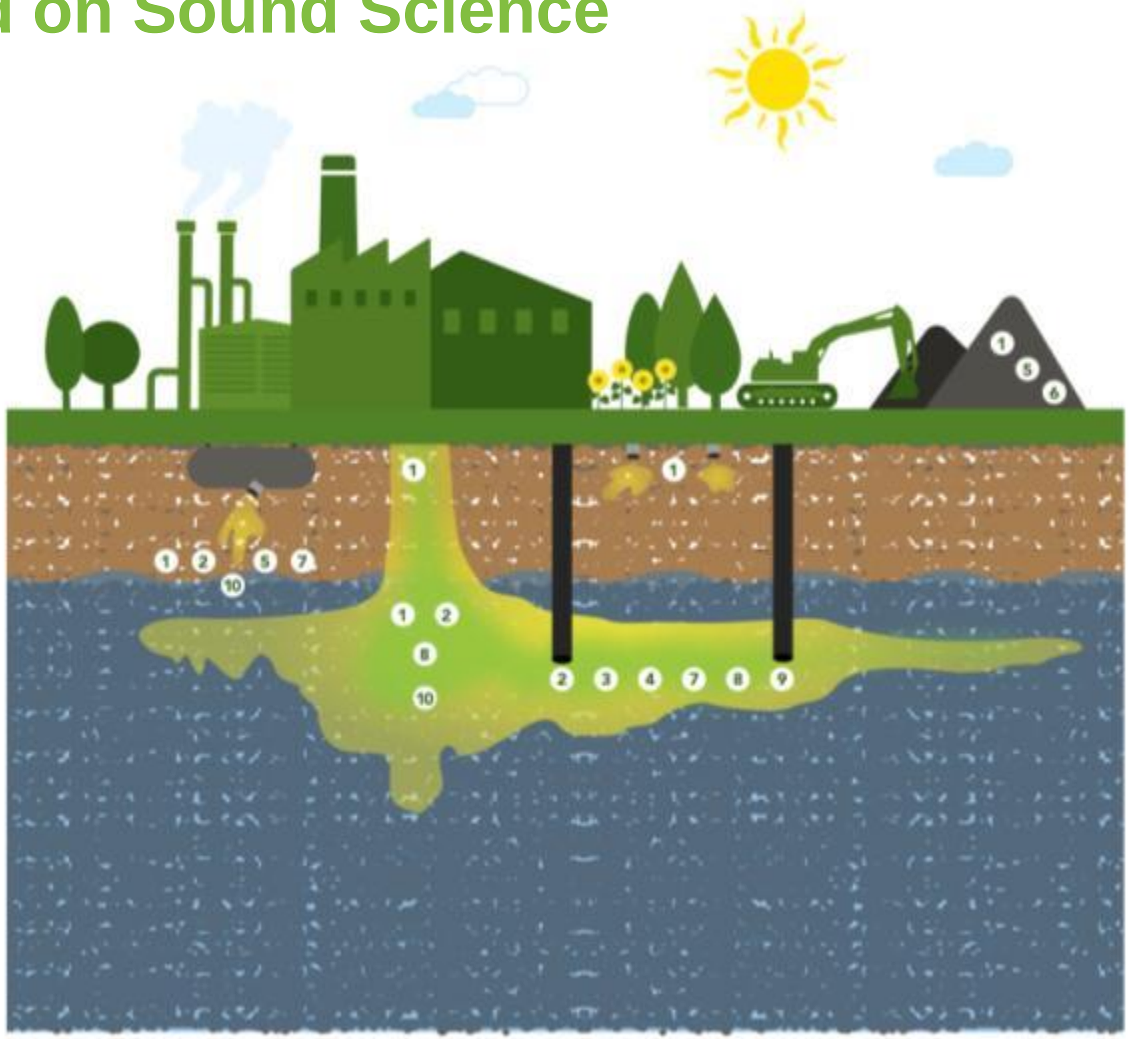
8. EHC® Metals and MetaFix® Reagent

***Enhanced Reductive Dechlorination***

9. ELS™ Microemulsion

***NAPL Stabilization/Mass Flux Reduction***

10. ISGS™ Technology



# Support We Provide

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- Expert Technical Team
- Field-Proven Technologies
- Field Support
- R&D and Treatability Laboratories
- Technical and Design Support
- Mixing and Handling Equipment

# Presentation Outline

- Klozur Persulfate
- Monitoring Programs
  - Science and Technologies
  - Prior to Field Applications
  - Field Applications
  - Lessons Learned
- Conclusions

# KLOZUR PERSULFATE

# Introduction to Klozur® Persulfate

## Klozur® Persulfate is:

- Environmental grade sodium persulfate:
  - A strong oxidant used for the destruction of contaminants in soil and groundwater
  - Highly soluble in water (significant oxidant mass is smaller volumes)
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants when properly activated

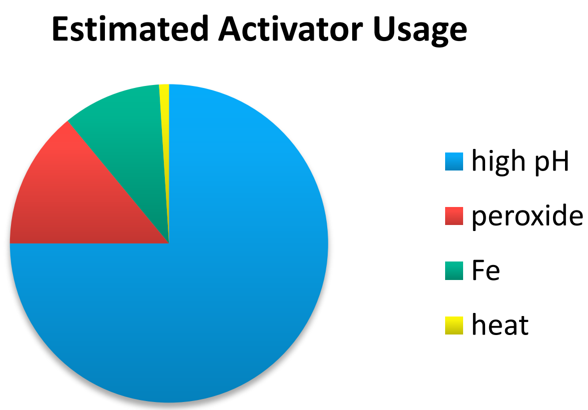

Theoretical solubility of more than 500 g/L. Injection concentrations of 50 to 250 g/L.

# Radical Formation Upon Activation

- Kinetically faster reacting radicals that are:
  - More powerful oxidants ($SO_4$• and OH•) than persulfate itself
  - Reductants ($O_2$•$^-$)
  - Nucleophiles ($O_2$•$^-$ and $HO_2^-$)

| Oxidant | Standard Reduction Potential (V) | Reference |
|---|---|---|
| Hydroxyl radical (OH•) | 2.59 | Siegrist et al. |
| Sulfate radical ($SO_4$•$^-$) | 2.43 | Siegrist et al. |
| Ozone | 2.07 | Siegrist et al. |
| Persulfate anion | 2.01 | Siegrist et al. |
| Hydrogen Peroxide | 1.78 | Siegrist et al. |
| Permanganate | 1.68 | Siegrist et al. |
| Chlorine (HOCl) | 1.48 | CRC (76th Ed) |
| Oxygen | 1.23 | CRC (76th Ed) |
| Oxygen | 0.82 | Eweis (1998) |
| Fe (III) reduction | 0.77 | CRC (76th Ed) |
| Nitrate reduction | 0.36 | Eweis (1998) |
| Sulfate reduction | -0.22 | Eweis (1998) |
| Superoxide ($O_2$•$^-$) | -0.33 | Siegrist et al. |
| ZVI | -0.45 | CRC (76th Ed) |

# Current Activators




- Alkaline Activated Persulfate
  - Well suited for suited for most applications
  - Less corrosion on carbon steel
  - Reductants, oxidants and nucleophiles
- Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and hydrocarbons
  - Oxidative pathway
- Heat
  - Complex sites
  - Polishing step after thermal treatment
  - Reductants, oxidants and nucleophiles
- Hydrogen Peroxide
  - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate
  - Reductants, oxidants and nucleophiles

# Compounds Degraded by ISCO

## Examples of Contaminants Destroyed by Klozur Persulfate

**Chlorinated Solvents**
PCE, TCE, DCE
TCA, DCA
Vinyl chloride
Carbon tetrachloride
Chloroform
Chloroethane
Chloromethane
Dichloropropane
Trichloropropane
Methylene chloride

**Others**
Carbon disulfide
Aniline
1,4-Dioxane

**TPH**
BTEX
GRO
DRO
ORO
creosote

**Oxygenates**
MTBE
TBA

**Perflourinated**
Freon
PFOS
PFOA
PFBA

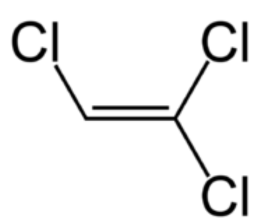
**Chlorobenzenes**
Chlorobenzene
Dichlorobenzene
Trichlorobenzene

**Phenols**
Phenol
Chlorophenols
Nitrophenols

**PAHs**
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
Trimethylbenzene

**Pesticides**
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

**Energetics**
Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



# SCIENCE AND TECHNOLOGIES

# Site Equilibrium

- Various contaminant phases are usually in equilibrium:
  - Groundwater
  - Soil
  - Non-Aqueous Phase Liquids (NAPLs)
  - Crystalline solids
  - Soil Vapor

- Soil and Groundwater:

$$Kd = Koc * foc = \frac{Conc\ on\ Soil}{Conc\ in\ GW}$$

- Where:
  - $K_d$ = Soil partitioning coefficient
  - $K_{oc}$ = Organic carbon partitioning coefficient
  - $f_{oc}$ = Fraction organic carbon in soils

# Common Monitoring Technologies

- Groundwater samples
- Soil samples
- High Resolution Site Characterization (HRSC) technologies
  - Membrane Interface Probe (MIP)
  - Luminance technologies

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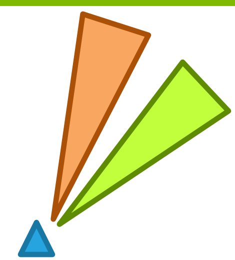
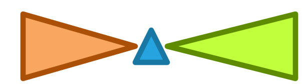
# Groundwater Sampling

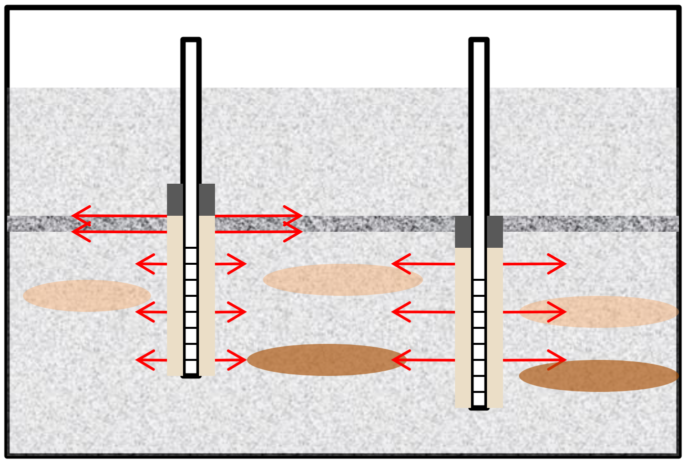
- Groundwater contamination usually in equilibrium with soil and, if present, NAPL
- Represents:
  - Up gradient conditions
  - Average or composite of screen interval
- Concentrations limited by theoretical solubility
  - Partitioning does not estimate equilibrium above solubility
- Common Methods
  - Purge
  - Low flow
  - Snap
  - Diffusion bag

Slight shift in GW direction



Flat GW gradients sometimes reverse





# Soil Sampling

- Higher $K_{oc}$, more mass usually on soil
- Prone to variability
- Collection method
- Types of Soil Samples
  - Grab
  - Composite

| Contaminant | GW (mg/L) | Foc | Koc | Soil (mg/Kg) | Percent (%) | |
|---|---|---|---|---|---|---|
| | | | | | GW | Soil |
| VC | 10 | 0.005 | 2.5 | 0.1 | 94% | 6% |
| DCE | 10 | 0.005 | 49 | 2.5 | 45% | 55% |
| TCE | 10 | 0.005 | 94 | 4.7 | 30% | 70% |
| PCE | 10 | 0.005 | 265 | 13.3 | 13% | 87% |

Notes: Dry bulk density 110 lbs/ft3
Porosity 0.35

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# High Resolution Site Characterization (HRSC)

- Probes typically mounted typically to direct push rods
  - Membrane interface probes (MIP): PID, ECD, XSD, FID, conductivity, and others
  - Laser Induced Fluorescence (LIF)
- Allows for a rapid indirect assessment of the site
  - 100-400 linear ft per day


*Courtesy of Cascade*

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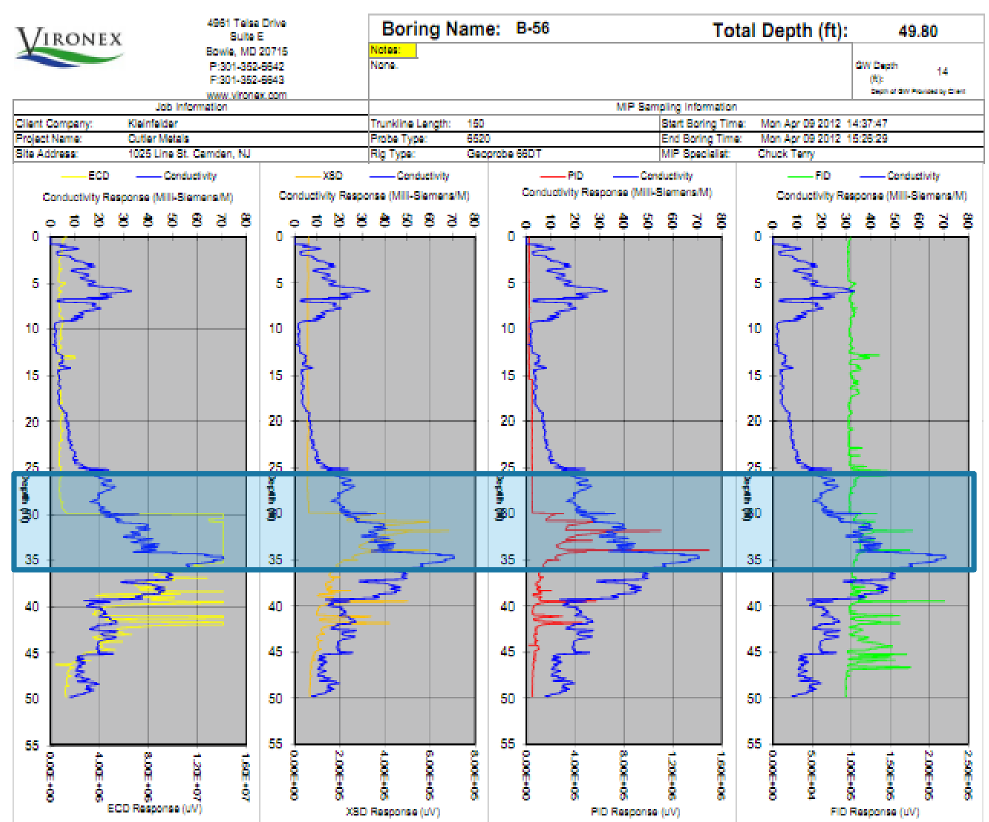
# MIP Data

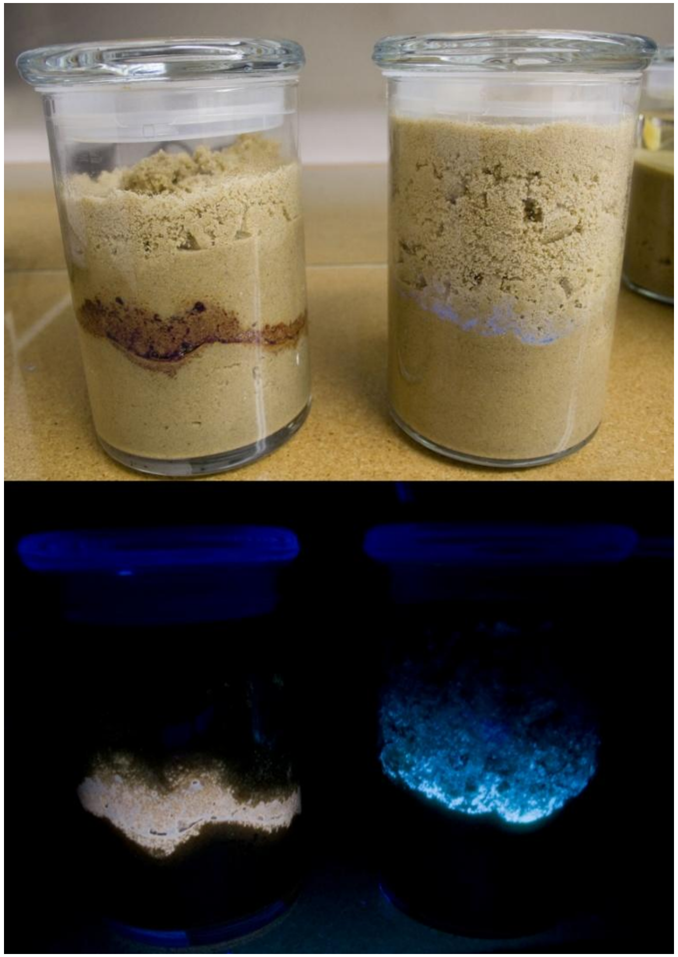
- Vertical site data
- Multiple points allow for horizontal evaluation
- Slower push rate results in highest sensitivity




*Courtesy of Cascade*

# Laser Induced Fluorescence

- Different frequency of lasers cause different petroleum hydrocarbon NAPLs to fluoresce.
- Detectors measure the magnitude of the fluorescence
- Output looks similar to MIP



https://clu-in.org/characterization/technologies/lif.cfm

# MONITORING PROGRAM

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# Monitoring Program

- Used to develop critical data at different steps in the remedial process:
  - Prior to a Field Application:
    - Conceptual Site Model (CSM)
    - Application Design
  - Field Application
    - Baseline
    - Application
    - Post-Application

# Data Requirements

- Different data required at each step
- Monitoring program usually set up to gather data to meet specific objectives



# Common Objectives

- Conceptual Site Model
  - Contaminant distribution
  - Site geology, hydrology and general site characteristics
- Klozur Field Application Design
  - Key design parameters
- Performance Monitoring
  - Progress toward remedial goals
  - Assessing effectiveness of ISCO application
- Application Monitoring
  - Understanding, documenting, and optimizing application event

# PRIOR TO A FIELD APPLICATION:

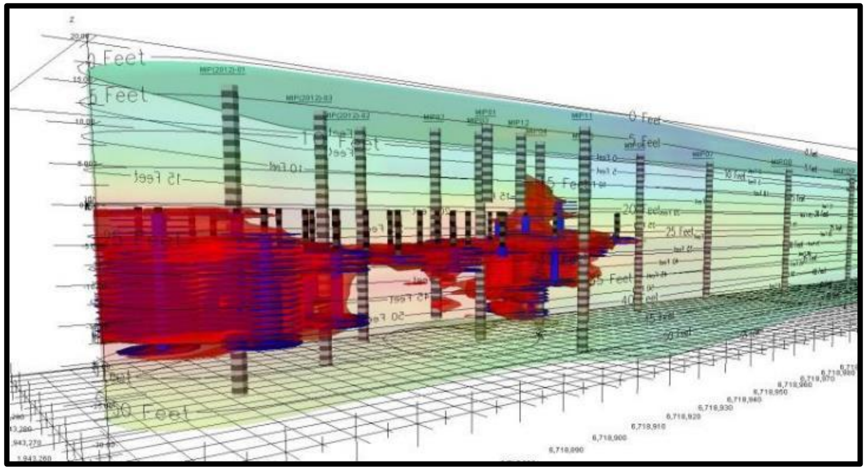
# CONCEPTUAL SITE MODEL AND APPLICATION DESIGN

# Conceptual Site Model

- First step in remedial approach
- Common Objectives:
  - Understand site characteristics
    - Contaminant
    - Site geology
    - Hydrology
    - Remedial goals
    - Site conditions and context
  - More detailed data, the better for remedial design
- Additional Considerations:
  - Be able to assess remedial alternatives
    - Oxidative vs. reductive treatment pathway
    - Concentration dependent treatment
  - Have sufficient data for design
    - Minimize need for additional (Data Gap) investigation

# Conceptual Site Model – Typical Parameters

- Contaminant Distribution Across Site:
  - Type(s)
  - Phase(s)
  - Concentrations in each phase across the site (g/L, mg/L and mass of NAPL)



**Considerations:**

- Need to know contaminant type, mass, and phase to understand how to establish contact and estimate necessary mass of oxidant

# Conceptual Site Model- Typical Parameters

- Vertical and horizontal extent:
  - Soil types and characteristics
  - Hydraulic conductivity
- Groundwater:
  - Velocity
  - Direction
  - Potential for seasonal variations
  - Geochemistry
    - DO, ORP, conductivity, and pH
    - Types and quantities of metals

Considerations:

- Soil conductivity and heterogeneity can effect ability to establish contact
- Helps in placement of injection locations (vertical interval)
- Groundwater velocity and direction impacts injection event and monitoring

# Conceptual Site Model- Typical Parameters

- General site characteristics
  - Surface features
  - Accessibility
  - Sensitive receptors
- Final and interim remedial goals

- Considerations:
  - Staging area
  - Equipment access
- Remedial goals are a key consideration in technology selection and design

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# Key to Success for Klozur Field Applications

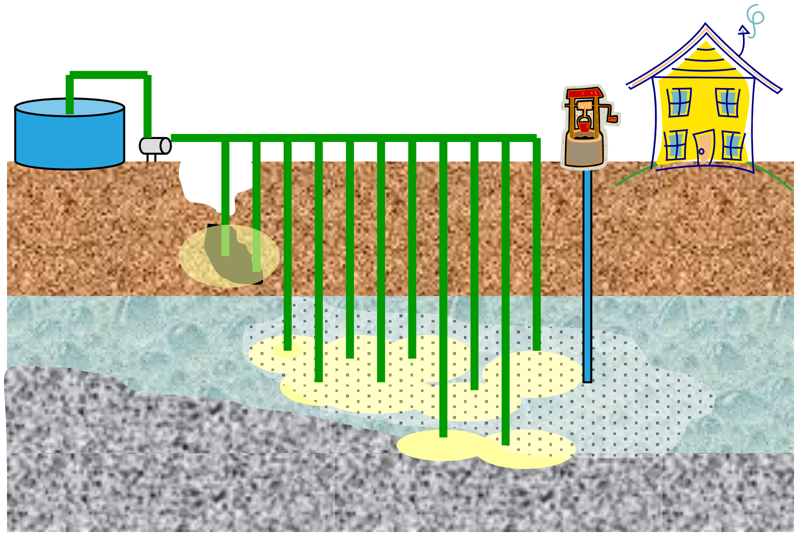
- Highly efficient reactions are known to take place on the laboratory scale
  - 100% contact between ISCO and contamination

- Scale up to the field:

ISCO works by establishing contact between a sufficient mass of activated oxidant with the contaminant mass in the subsurface.

# Klozur Persulfate Application Design Parameters

- Data typically needed for an ISCO Design
- Common Objectives:
  - Have data needed to develop an field application design
  - Compare against other technologies



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# Data Needed for Design: Oxidant Demand

**$[(CM_{Soil} + CM_{GW} + CM_{NAPL}) \times Ratio + SOD * Soil\ Mass] \times S.F.$**

- Target Volume
  - Well defined/refined target area
- Contaminant
  - Groundwater concentration
  - Soil concentration
  - NAPL
- Soil characteristics:
  - Soil density
  - Porosity
  - Foc
- Bench tests
  - Soil oxidant demand (SOD)
  - Base buffering capacity (BBC)

S.F. = Safety Factor
CM = Contaminant Mass

- Considerations:
  - Refined target volume can be used to optimize oxidant demand
  - Bench scale tests are used to provide critical design parameters
  - Accurate soil values vs assumptions can make significant difference

# Data Needed for Design: Establishing Contact

- Direct Injection- Subsurface Conditions:
  - Hydraulic conductivity
  - Groundwater flow (direction and velocity)
  - Soil type(s)
  - Effective porosity
  - Type and degree of soil heterogeneity
  - Contaminant vs. soil type distribution

- In Situ Mixing
  - Soil type(s)
  - Type and degree of soil heterogeneity

- Direct Injection Considerations:
  - Push reagents into formation to establish contact
  - Anticipated injection rate
  - Injection location screen placement
  - Consider percent of effective pore volume in design

- In Situ Soil Mixing Considerations:
  - Dewatering following application
  - Blended soil characteristics

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# Sequence of Monitoring Events

- Optimize monitoring
  - Focus in on refining target area
  - Collect design data while developing and refining CSM
- Optimized Sequence:
  - Widespread soil and gw samples
  - HRSC
  - Focused soil and GW samples from expected target area
    - Monitoring wells screened in target interval
    - Design data

# FIELD APPLICATIONS:

# PERFORMANCE AND APPLICATION MONITORING

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# Performance Monitoring

- What is it:
  - Baseline and post-application monitoring
- Typical objectives:
  - Monitoring to assess the effectiveness of the application
  - Progress toward remedial goals

*Courtesy of XDD and NAVFAC*

# Performance Monitoring: Typical Parameters

- Full scale or Pilot Test

- Evaluative/Iterative approach
  - Monitor between events to optimize multiple applications

- Parameters to be evaluated before and after application to be selected based upon how a site is to be evaluated
  - Assess effectiveness of Application
  - Progress toward remedial goals

- Typical Parameters:
  - Groundwater
    - Contaminant(s)
    - Geochemical (Dissolved oxygen, ORP, conductivity, pH, temperature, etc)
    - Residual Oxidant
    - Others (metals)
  - Soil
    - Contaminant(s)
    - $f_{oc}$
  - Residual NAPL
  - MIP/HRSC

$$Kd = Koc * foc = \frac{Conc\ on\ Soil}{Conc\ in\ GW}$$

# Performance Monitoring: Frequency

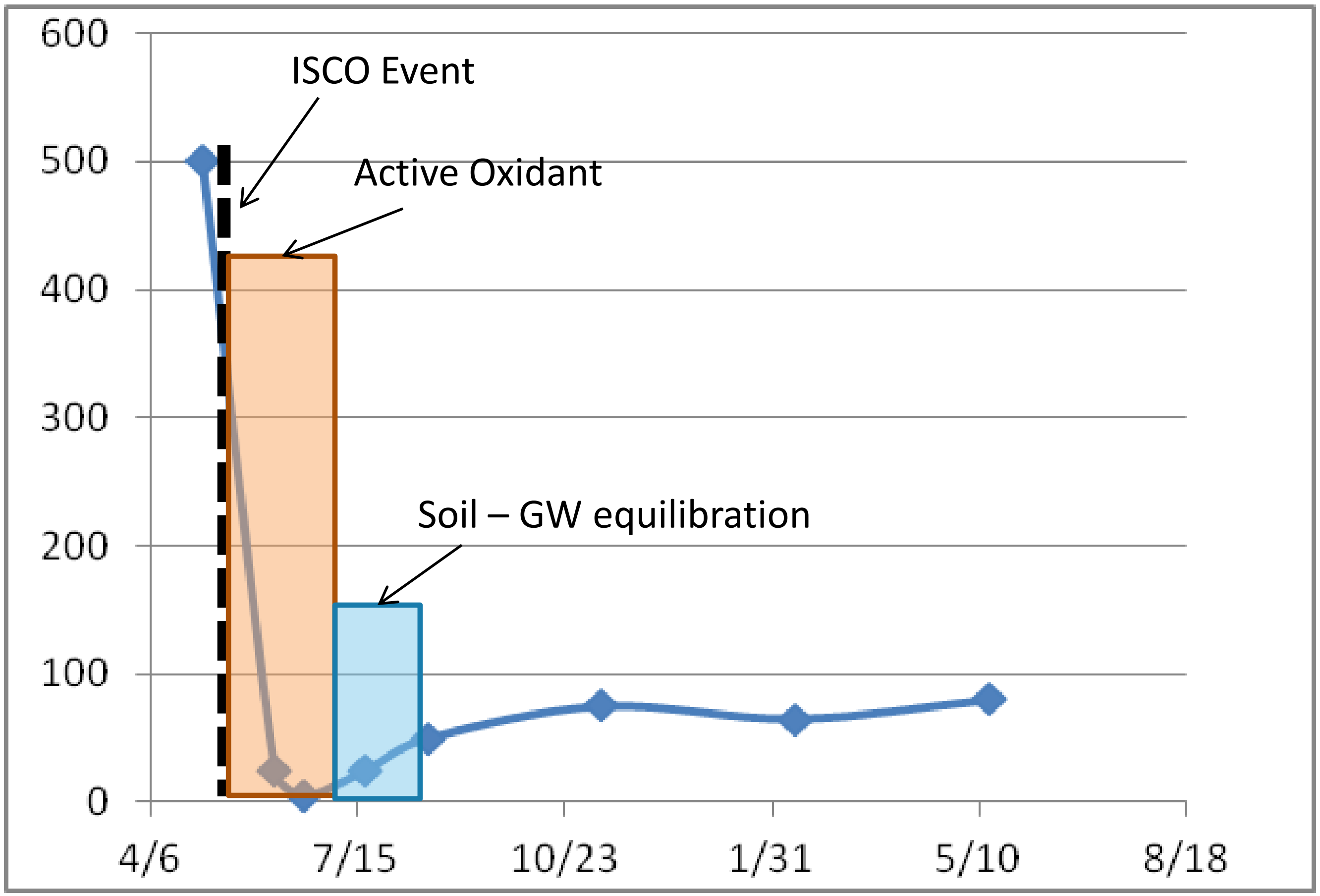
- Baseline:
  - Groundwater:
    - Within 1 month prior of injection typical
    - Multiple baseline events would help identify trends
  - Soils
    - Typically with well installation

Remedial goals are often associated with groundwater; however, assessing the effectiveness if an application solely on soil based data (sampling and/or MIP/HRSC) may be necessary

- Post Application
  - Groundwater:
    - Dependent on goals
    - Multiple events would help assess equilibrium
    - If single event: 2-3 months typical for contaminants
    - Potentially longer for geochemistry and metals (if applicable)
  - Soils
    - Once majority of oxidant is consumed

# Performance Monitoring: Frequency

**Hypothetical Event**



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# Performance Monitoring: Pilot Tests

- Pilot Tests/Design Optimization
  - Subset of larger area
  - First application in small area
- Objectives of Pilot Tests:
  - Confirm treatment
  - Evaluate design parameters
- Critical Field Parameters
  - Treatment efficacy
  - Injection rate
  - Injection pressure
  - Distribution of reagents
    - Active oxidant
    - Inactive oxidant
  - Potential issues
- Monitoring program
  - Typically more extensive than full scale
  - Intended to monitor treatment efficacy and field parameters

# Application Monitoring

- What is it:
  - Monitoring during the field event/application
- Typical objectives:
  - Control system during application
  - Ability to describe field event (historical record)
  - Confirm design assumptions
  - Understand the distribution of the reagents

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# Application Monitoring: Typical Parameters

- Batching and Injection System:
  - Batching records (volume and mass)
  - Concentrations of stock solution feeds
  - Flow rates and pressures of stock solution feeds
  - Geochemical parameters and oxidant concentration of injection solution
- Injection Location/Wells:
  - Injection rate for each injection location
  - Injection pressure at wellhead
- Mass of Klozur and other reagents applied at each interval and location
- Monitoring Wells
  - Field measurement of geochemical parameters
  - Residual oxidant of injection solution
- Onsite Occurrences of Note
  - Surfacing of reagents
  - Start and stop times
  - Delays
  - Inclement weather

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# Application Monitoring: Frequency

- Monitor as needed
  - Batching System: Each Batch
  - Injection system parameters: Multiple times a day
  - Monitoring wells: Multiple times per event
  - Occurrences of Note: As necessary

# Data Assessment

- Active oxidant
  - Contains activated Klozur persulfate
  - Presence of persulfate confirmed with field test kits
- Inactive reagent solution
  - Does not contain activated Klozur persulfate
  - Conductivity or sodium used as indicator
- Peroxychem Klozur Field Test Kits
  - Calibrated for typical Klozur application concentrations (1 g/L to 100 g/L)
  - Reverse titration minimizes potential interferences

# LESSONS LEARNED

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# Changes in Foc

- Klozur oxidizes naturally occurring organics
  - Component of SOD
- Foc typically decreases by a significant amount
  - Can have significant reductions in contaminant mass with little to no change in GW concentrations
- Key:
  - ISCO reduces contaminant mass
  - Understand all relevant phases and changes in $f_{oc}$

$$Kd = Koc * foc = \frac{Conc\ on\ Soil}{Conc\ in\ GW}$$

| Contaminant | GW (mg/L) | Foc | Koc | Soil (mg/Kg) | Total Mass (mg) | Percent (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reduction | GW | Soil |
| VC | 10 | 0.005 | 2.5 | 0.1 | 105 | | 94% | 6% |
| DCE | 10 | 0.005 | 49 | 2.5 | 221 | | 45% | 55% |
| TCE | 10 | 0.005 | 94 | 4.7 | 334 | | 30% | 70% |
| PCE | 10 | 0.005 | 265 | 13.3 | 760 | | 13% | 87% |

Notes: Dry bulk density 110 lbs/ft3
Porosity 0.35

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| | | | | | | Reduction | GW | Soil |
| VC | 10 | 0.0005 | 2.5 | 0.0 | 100 | 5% | 99% | 1% |
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|---|---|---|---|---|---|---|---|---|
| | | | | | | Reduction | GW | Soil |
| VC | 4 | 0.0005 | 2.5 | 0.0 | 40 | 62% | 99% | 1% |
| DCE | 4 | 0.0005 | 49 | 0.1 | 45 | 80% | 89% | 11% |
| TCE | 4 | 0.0005 | 94 | 0.2 | 49 | 85% | 81% | 19% |
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Notes: Dry bulk density 110 lbs/ft3
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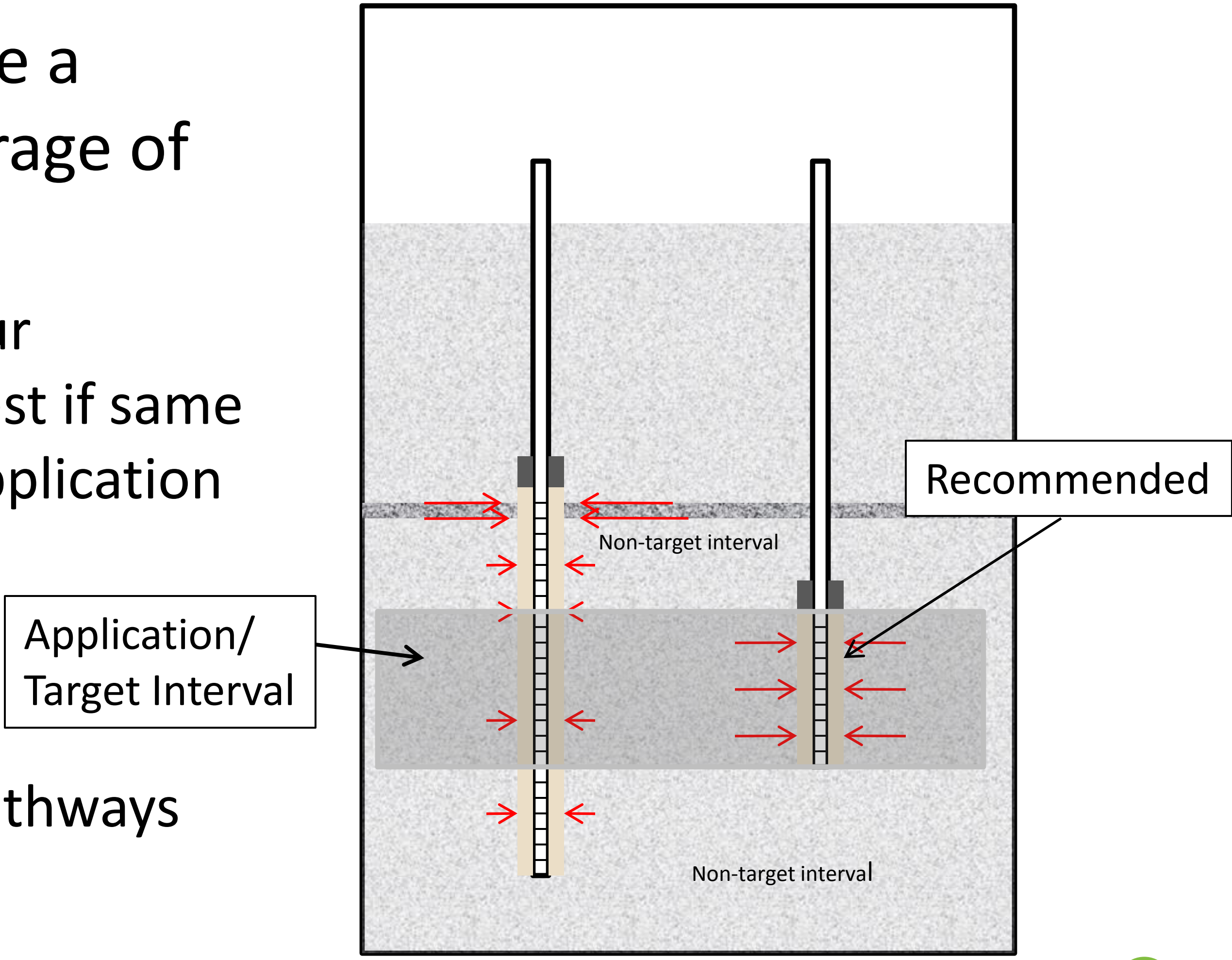
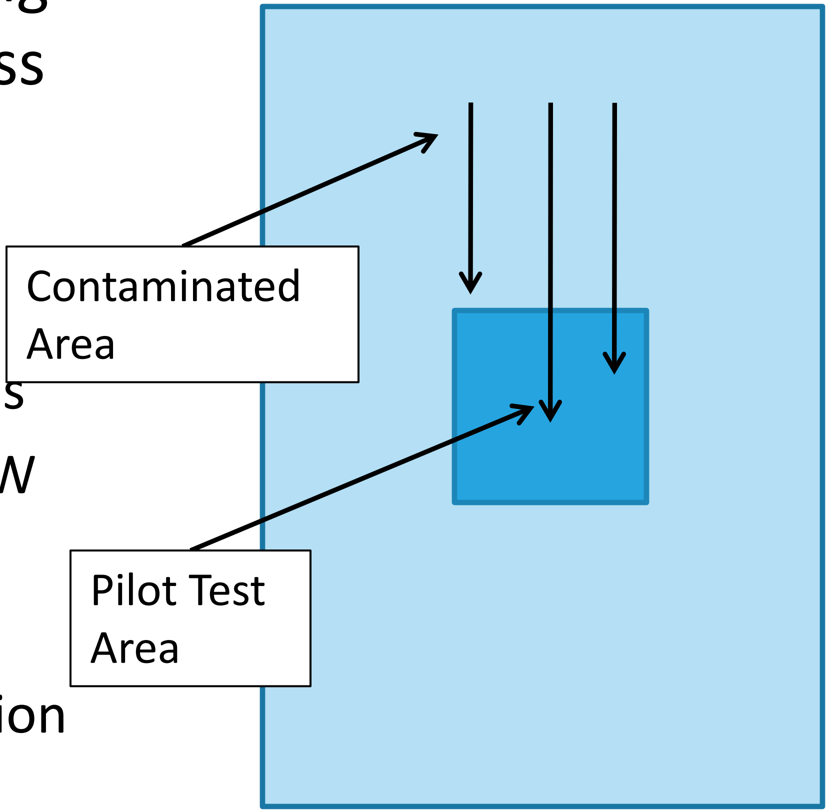
# Well Screens

- Well screens are a composite/average of screen interval
  - To assess Klozur application, best if same or subset of application target interval
  - Can still favor preferential pathways



# Groundwater Velocity

- Groundwater monitoring wells represent soil mass some distance up gradient of well
  - Can be recontaminated from up gradient sources
  - Sampling schedule vs GW velocity
  - MW location
  - Up gradient contamination



# SUMMARY AND CONCLUSIONS

# Summary and Conclusions

- Monitoring Program is an important aspect of a remedial approach
- Program should be carefully considered to fit site needs
- Having accurate and refined data will help with accurate design
- Klozur persulfate is a mass reduction technology and it is best to understand changes in all contaminant phases to assess effectiveness
- Reference: https://clu-in.org/characterization/

# Thank You - Questions

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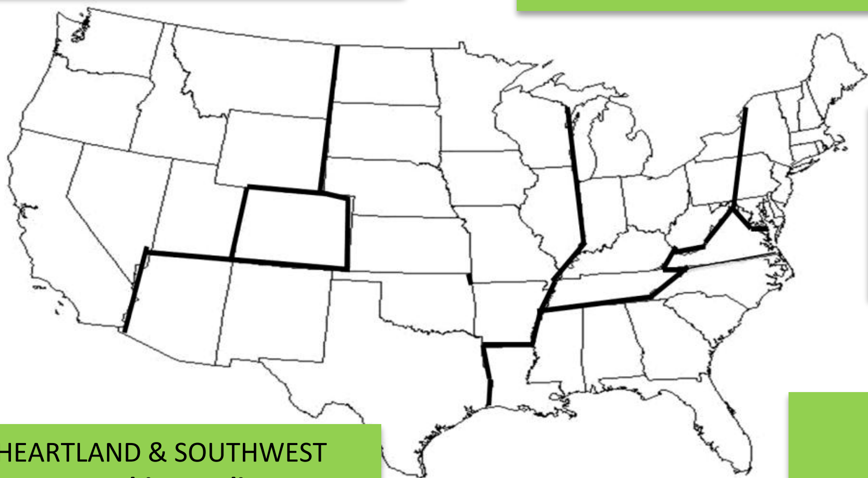

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