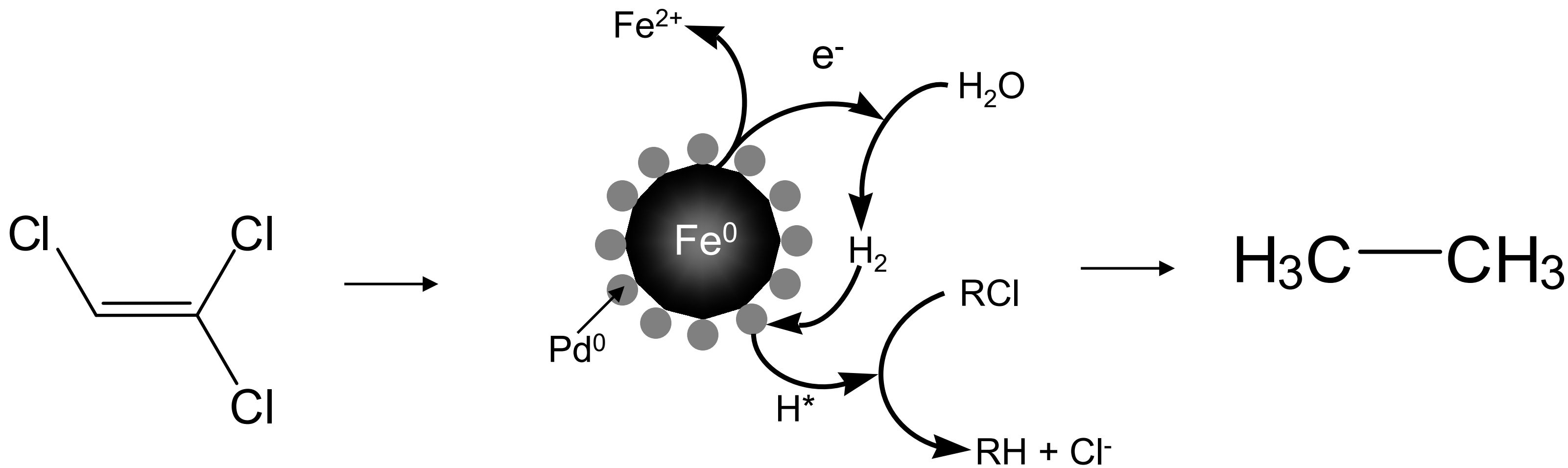
PGDP Nano-Particle Remediation Project



Center for Applied Energy Research

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Kentucky Water Research Institute

PGDP Nano-Particle Remediation Project

Project Team Kickoff Meeting

October 28, 2009

OUTLINE

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PGDP Nano-Particle Remediation Project University Project Participants

Dr. Rodney Andrews	UK/CAER (Director)
Dr. Lindell Ormsbee	UK/KWRRI (PI)
Dr. David Sedlak	University of California Berkeley (PI)
Dr. DB Bhattacharyya	UK/Chemical & Materials Eng. (PI)
Scott Lewis	UK/Chemical & Materials Engineering
Noah Meeks	UK/Chemical & Materials Engineering
Dr. Vasilie Smuleac	UK/Chemical & Materials Engineering
Steve Hampson	UK CAER/KRCEE (PM)

PGDP Nano-Particle Remediation Project
University Project Participants

Supplemental Funding from

NIEH Superfund Basic Research Program (SBRP)

UC Berkeley – Sedlak

UK Ky. Water Resources – Ormsbee

UK Chemical & Materials Engineering – Bhattacharyya

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UK/KRCEE & UK/ChemE Technical Background

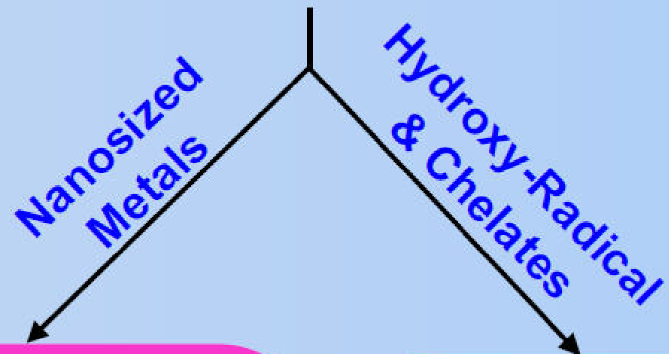
UK/ChemE Technical Background
Laboratory Studies - Phase 1 KRCEE Funding

Objectives

- Development of **effective methods** for the dechlorination of toxic organics
- Determine role of **dopant metal** in bimetallic nanoparticle reactivity
- Study potential for **on-site generation** of chemicals needed for chelate-modified Fenton reaction
- Determine effectiveness of both **reductive and oxidative dechlorination** in column studies to simulate groundwater flow

UK/ChemE Technical Background

Removal of TCE at Ambient Temperature



Reductive Dechlorination of TCE

(nano)Fe^0 + TCE → Fe^{2+} + Ethane + $3Cl^-$

(Bulk)Fe^0 + TCE → Fe^{2+} + intermediates + nCl^-

Systems Used:
Zerovalent metals (**Fe**), Bimetallic systems (**Fe/Pd, Fe/Ni**), Supported Platforms

Oxidative Destruction of TCE

TCE + $OH^{\cdot}$ → CO_2 , Organic Acids

Systems Used:

Standard Fenton Reaction,

Modified Fenton Reaction using **nontoxic chelate (citrate, gluconic acid) (L)** as a chelating agent (**FeL**).

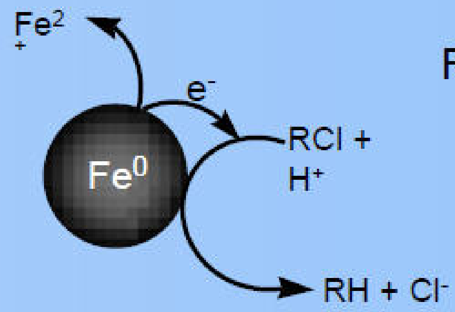
UK/ChemE Technical Background

Reductive Methods – Nanoparticle Background

- Nanoscale Metals Characteristic length < 100 nm
- Chloro-organic degradation rate increases 1-2 orders of magnitude over larger Fe particles
  - Increase in reactive surface area per reactant volume
- Minimal intermediate formation
- The use of a bimetallic system (Fe + Pd or Ni, etc.) increases the reactivity of the particle surface by incorporating a second metal
  - Second metal typically acts as hydrogenation promoter
- H also reacts to destruct chloro organic compounds
- 2nd Metal also
  - Reduces particle-soil interactions of Fe and
  - Increases in-situ particle mobility
- Evaluated aerobic and anaerobic groundwater & range of pH values
- Used RGA Groundwater
- Used RGA Matrix

Mechanism of Reductive Dechlorination

Single Fe^0 system



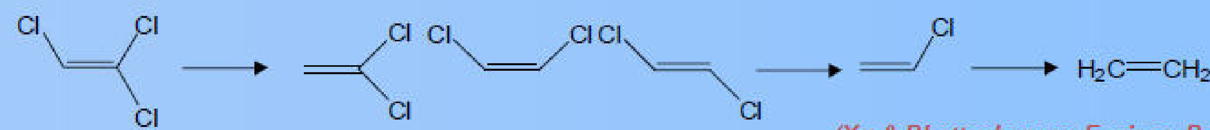
Reaction mechanism: electron transfer

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

$RCl + 2e^- + H^+ \rightarrow RH + Cl^-$

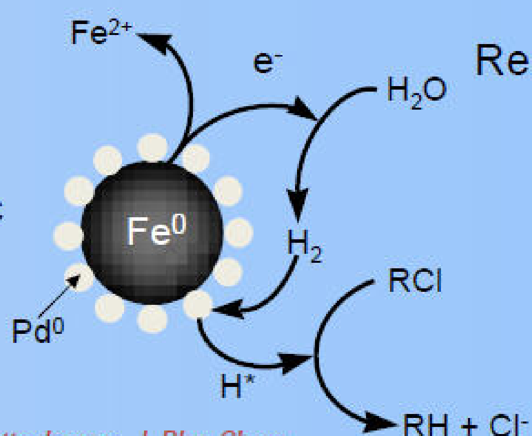
$RCl + Fe^0 + H^+ \rightarrow Fe^{2+} + RH + Cl^-$

(Matheson et al., Environ. Sci. Technol. 28, 2045-2053, 1994)



(Xu & Bhattacharyya, Environ. Prog., 24, 358, 2005)

Bimetallic system

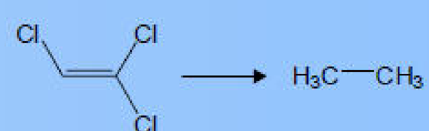


Reaction mechanism: catalytic hydrodechlorination

$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$

$H_2 + Pd \rightarrow Pd\text{-}H + H^*$

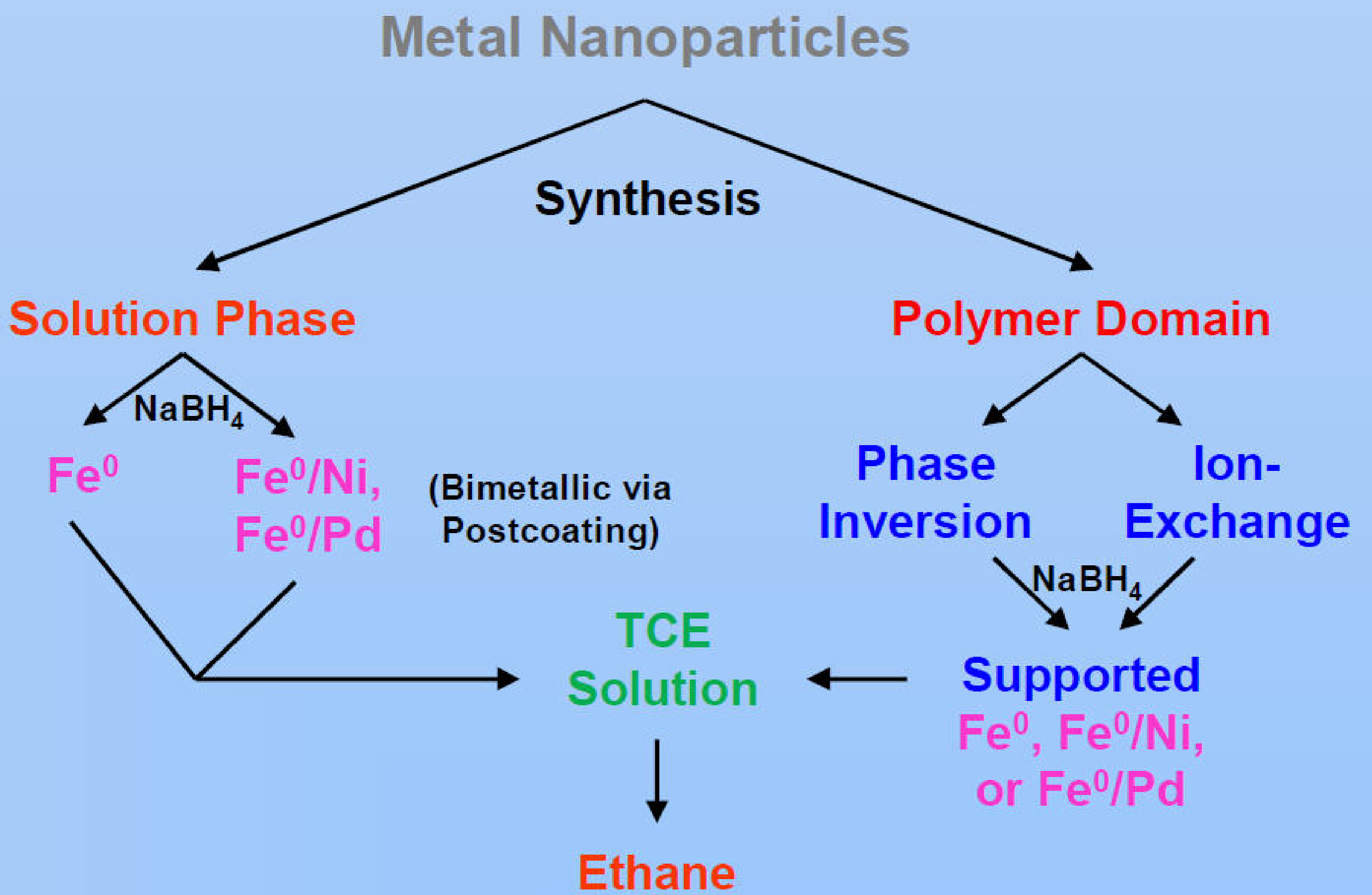
$RCl + H^* \rightarrow RH + Cl^-$



(Meyer and Bhattacharyya, J. Phy. Chem, 2007;Xu et al, J.Nanopar.Res. 7, 449-467, 2005)

UK/ChemE Technical Background

Reductive Dechlorination of TCE



UK/ChemE Technical Background

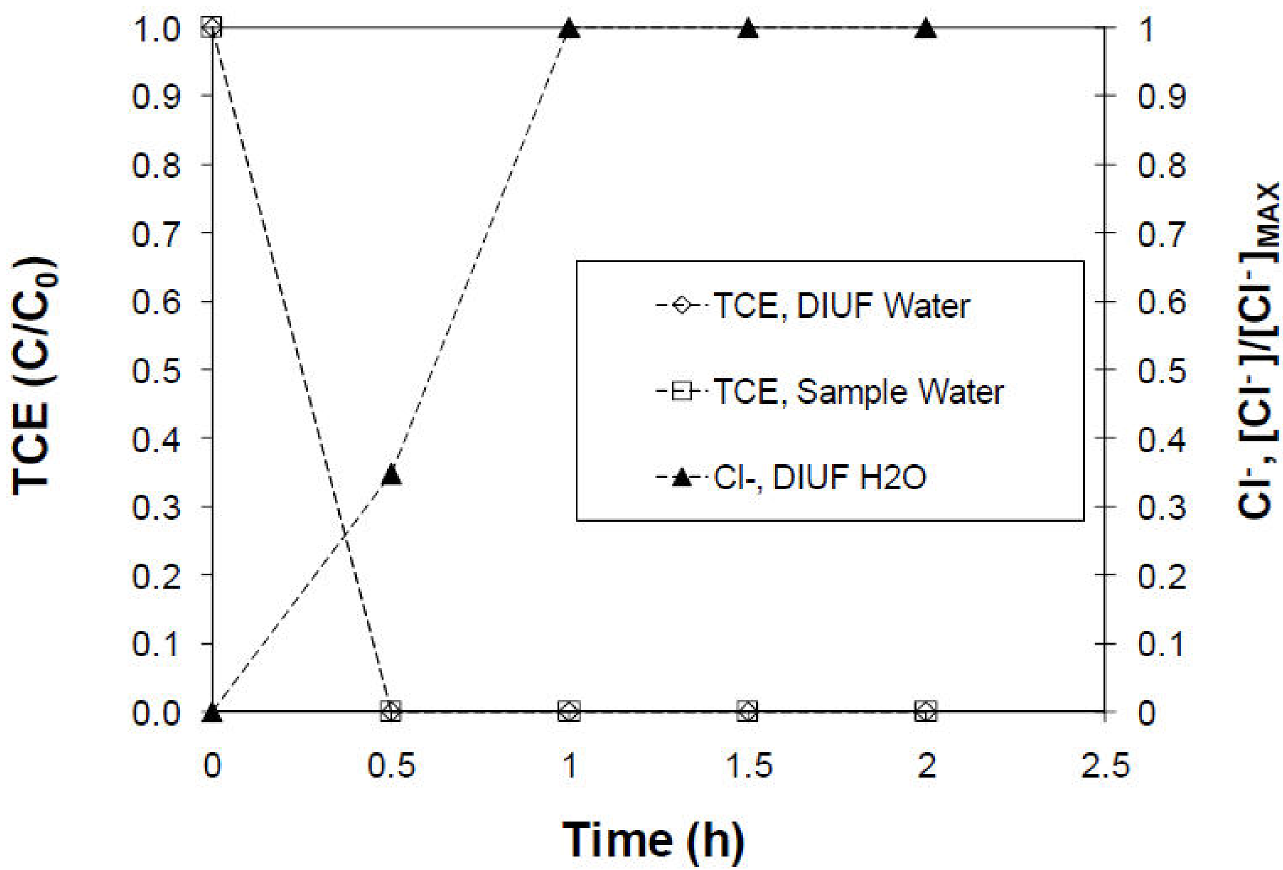


Figure 3. Evaluation of Pd/Fe nanoaggregates (0.8-wt% Pd) for the ideal dechlorination of 16.6 $mg.L^{-1}$ TCE at pH 6 using 1.0 $g.L^{-1}$ metal loading.

UK/ChemE Technical Background

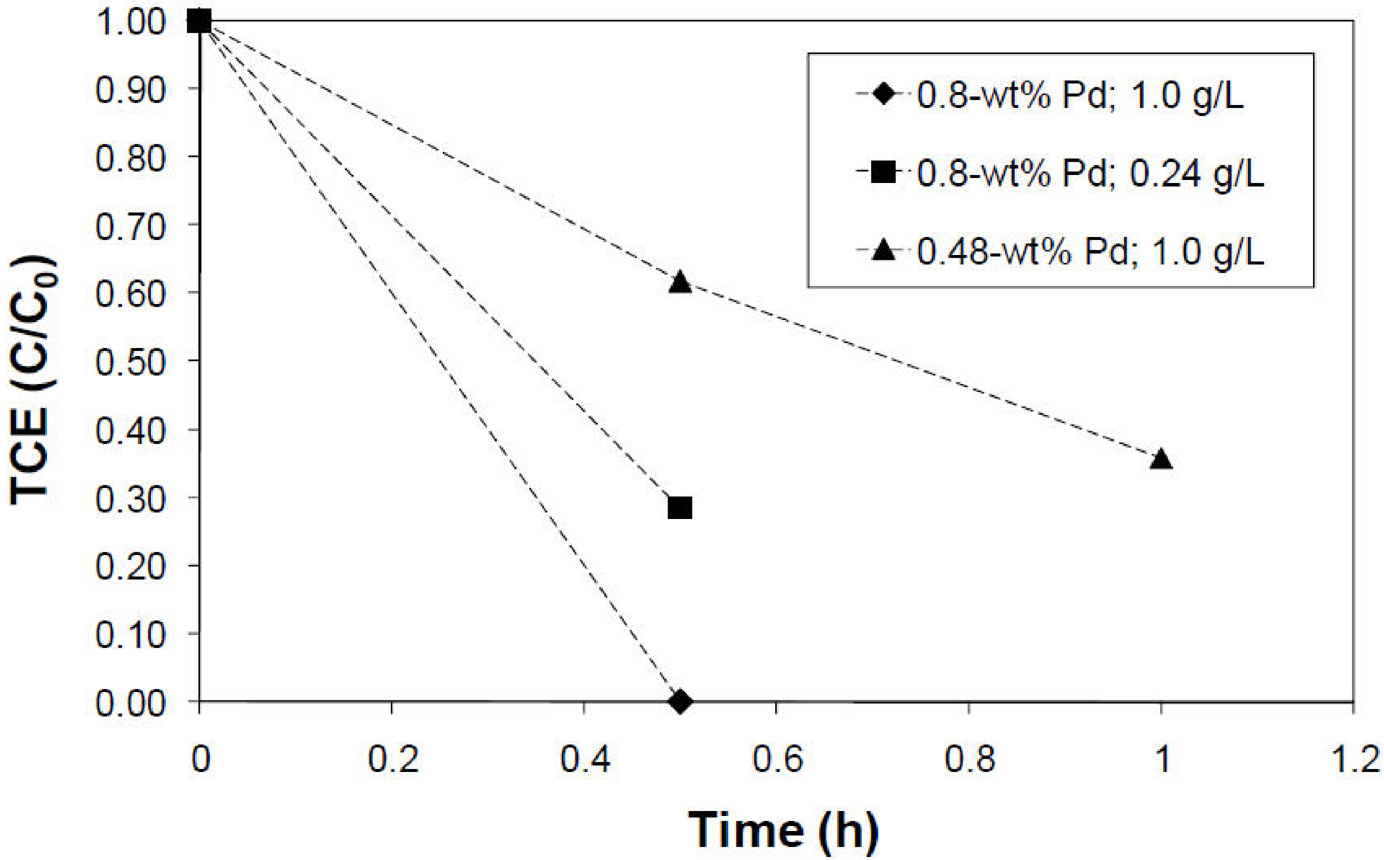


Figure 4. Examination of the effects of metal loading and Pd-deposition on the dechlorination of 20.5 mg.L^{-1} TCE in de-oxygenated DIUF water at pH 5.

UK/ChemE Technical Background

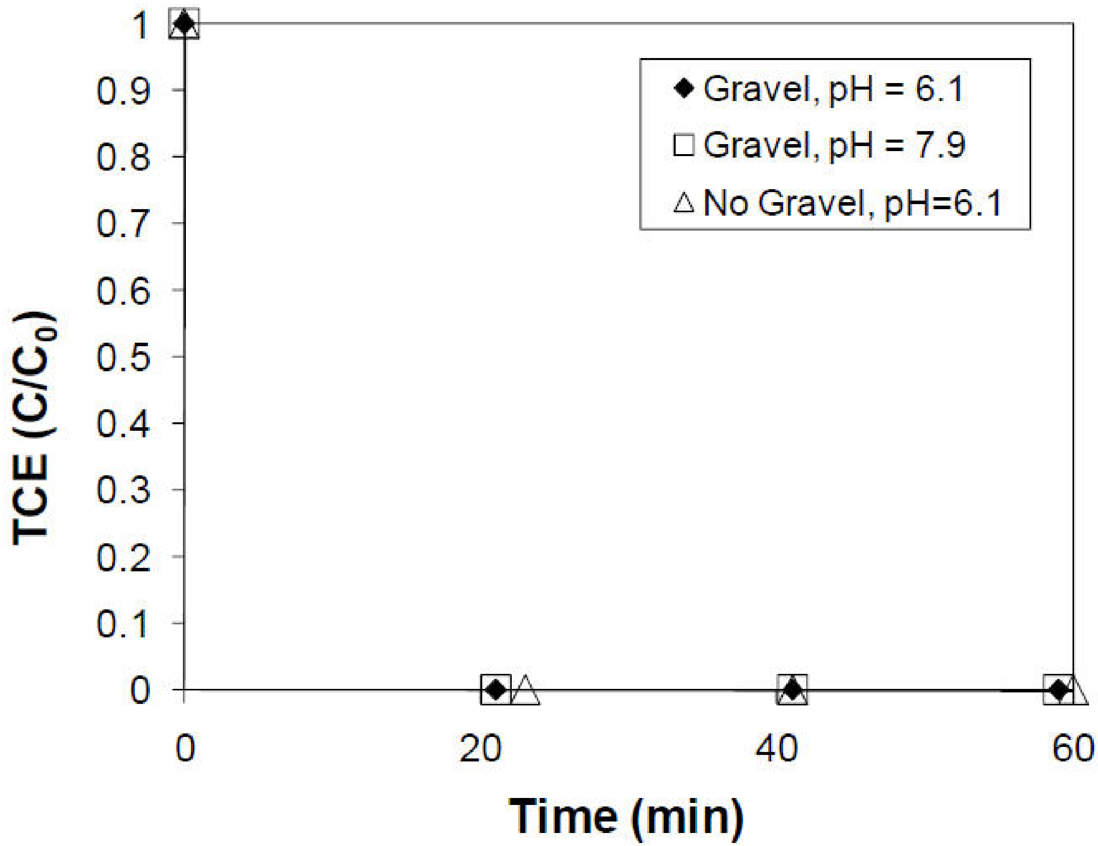


Figure 5. Reduction of a 21.1-mg.L^{-1} TCE solution in Paducah sample water under aerobic conditions in the presence of aquifer gravel using 0.9 g.L^{-1} of Fe nanoaggregates post-coated with 0.5-wt% Pd.

UK/ChemE Technical Background

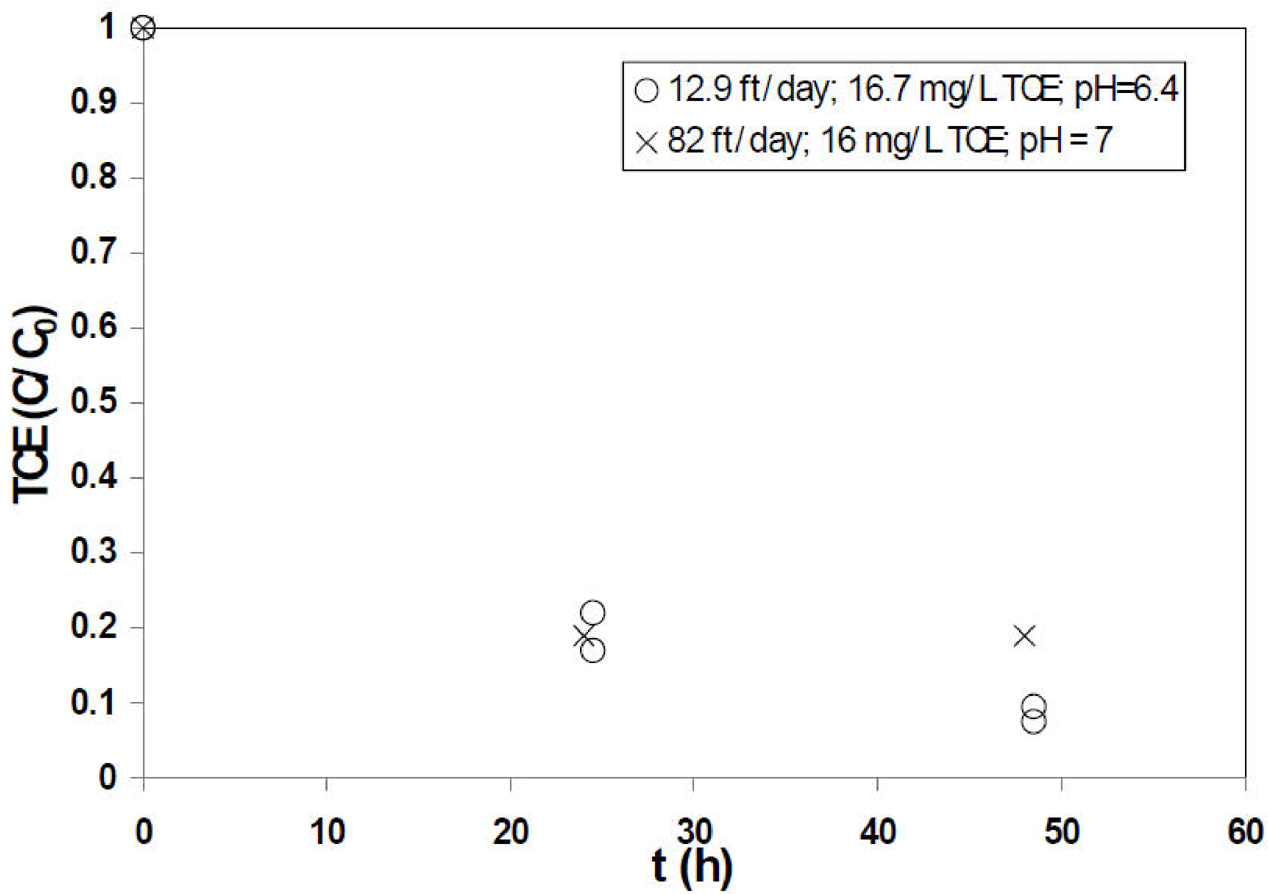


Figure 9. Results for circulating column dechlorination of TCE (C_0 = ~16 $mg.L^{-1}$ TCE) at pH 6.4-7 using 0.5 $g.L^{-1}$ of Fe/Pd nanoaggregates (0.4-wt% Pd) showing the negligible effects of groundwater velocity over the range of 12.9-82 ft per day.

UK/ChemE Technical Background

Reductive Methods – Bimetallic Nanoparticles

- Increasing 2nd metal surface loading will eventually result in a decline in the hydrogen generation rate
    - Lack of available exposed Fe surface area for corrosion.
- The influence of pH on hydrogen generation is insignificant over a broad range (5-8),
    - Indicates capability for dechlorination over this range.
- Dechlorination rates involving bimetallic systems are more accurately represented as a strong function of the rate of Fe corrosion with water because
    - The corrosion-generated hydrogen interacts with the 2nd metal (Pd, Ni, etc.) to form highly active H where it undergoes reaction with chloro-organics.
- This is a significant finding that will allow for more accurate modeling of ground water remediation involving bimetallic systems.
- TCE Destruction rates from 60 to 100% over a range of pH, TCE concentrations, times, dopant variations, Oxygen conditions, source water

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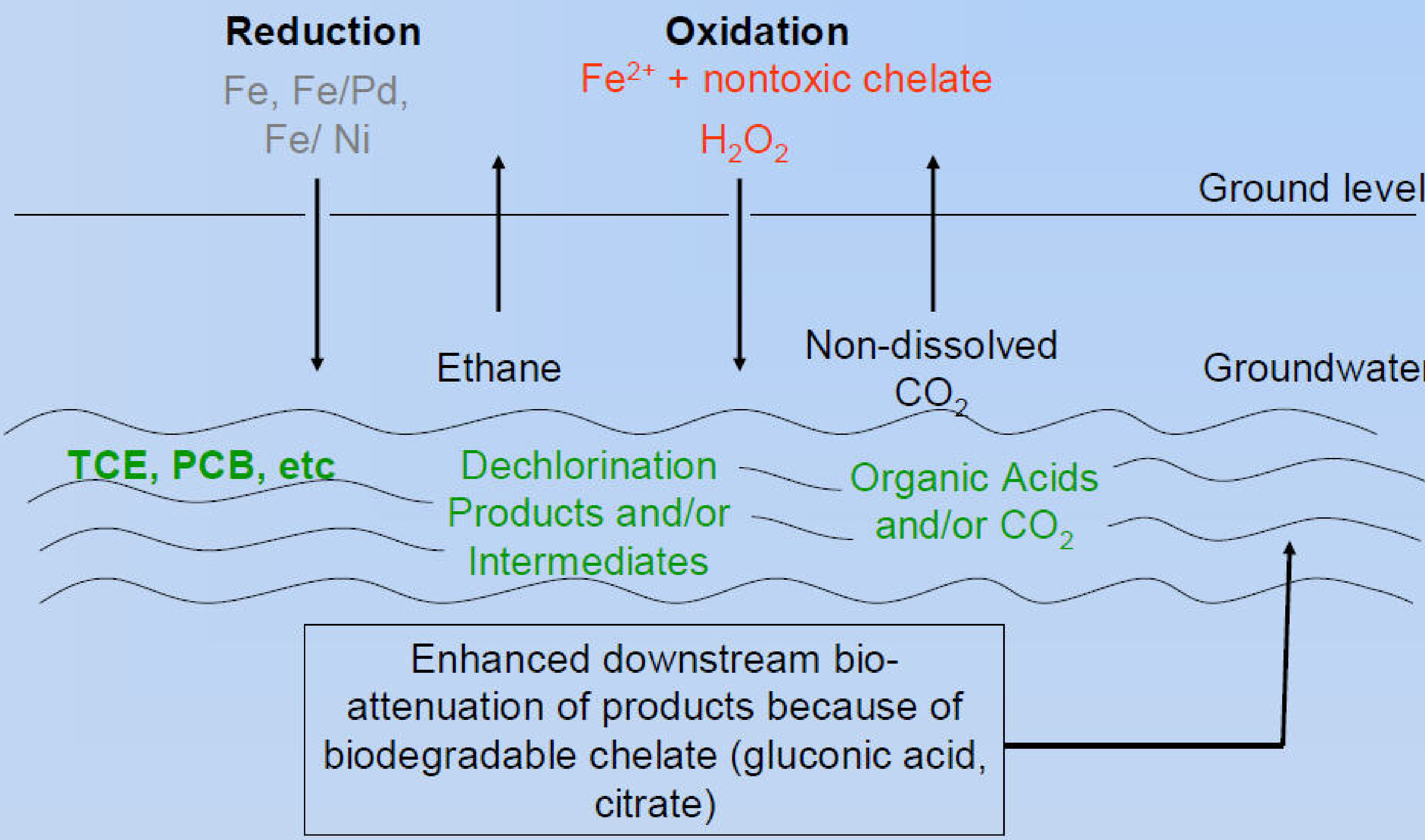
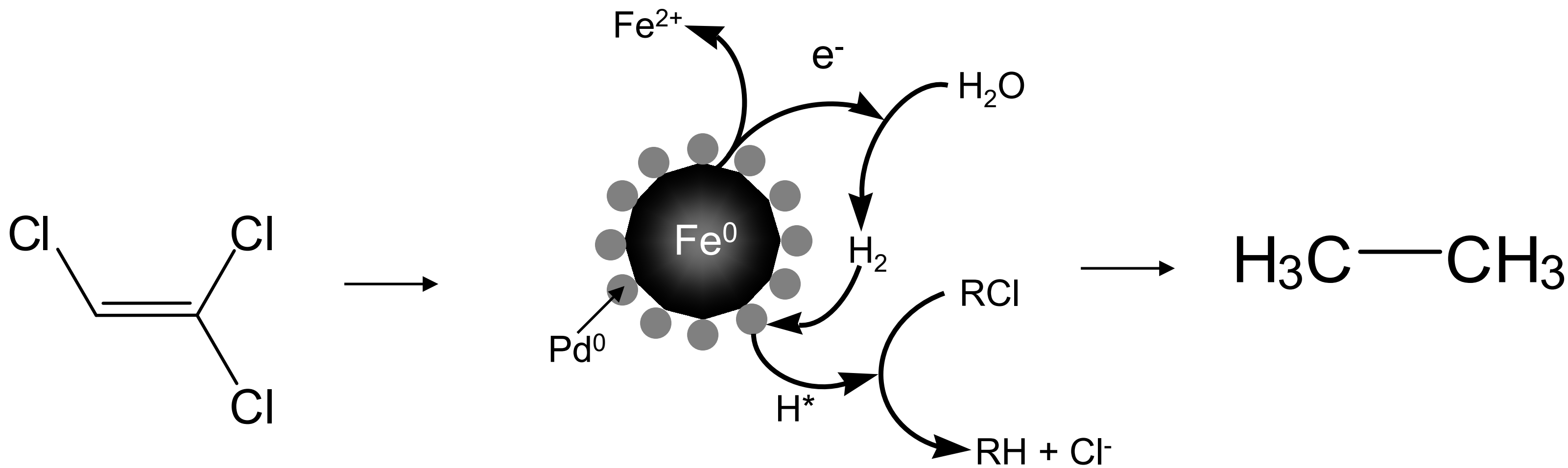
UK/ChemE Technical Background

Groundwater Remediation Using Combined Strategies For Reduction and Oxidation



PGDP Nano-Particle Remediation Project



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Dr. Vasilie Smuleac	UK/Chemical & Materials Engineering
Steve Hampson	UK CAER/KRCEE (PM)
	USEPA Region IV
	Ky. EEC
	Paducah Remediation Services
	DOE PPPO & PRC

PGDP Nano-Particle Remediation Project
Preliminary Project Schedule

Preliminary Project Schedule		
Activity	Start	Completed
UK Project Kickoff	5/1/2009	5/1/2009
UK Project Planning	5/1/2009	9/30/2009
Project Meeting with EPA-Cinn.	9/28/2009	9/28/2009
PROJECT TEAM KICKOFF	10/28/2009	
TS Workplan DQO	11/13/2009	11/25/2009
D1 Draft TS Workplan Start	11/13/2009	
D1 TS Workplan Completed	11/25/2009	12/17/2009
D1 Draft TS Workplan Review	12/17/2009	
D1 TS Workplan Revisions	12/18/2009	1/30/2009
D1 Submitted to DOE	1/30/2009	

PGDP Nano-Particle Remediation Project

Objective:

"Develop A Treatability Study Workplan for Nano Particle GW Pilot Demonstration at the PGDP"

- **Complete within timeframe to support DPP activities**
- **Address implementation, applicability, effectiveness, environmental stability of particles, aquifer geochemical impacts, & health and safety for proposed TS work**

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Treatability Study

- Treatability studies are laboratory or field tests designed to provide critical data needed to evaluate and, ultimately, to implement one or more treatment technologies. Factors that influence the type or level of testing include:
  - Phase of the project (i.e. RI/FS or RD/RA)
  - Technology-specific factors
  - Site-specific-factors

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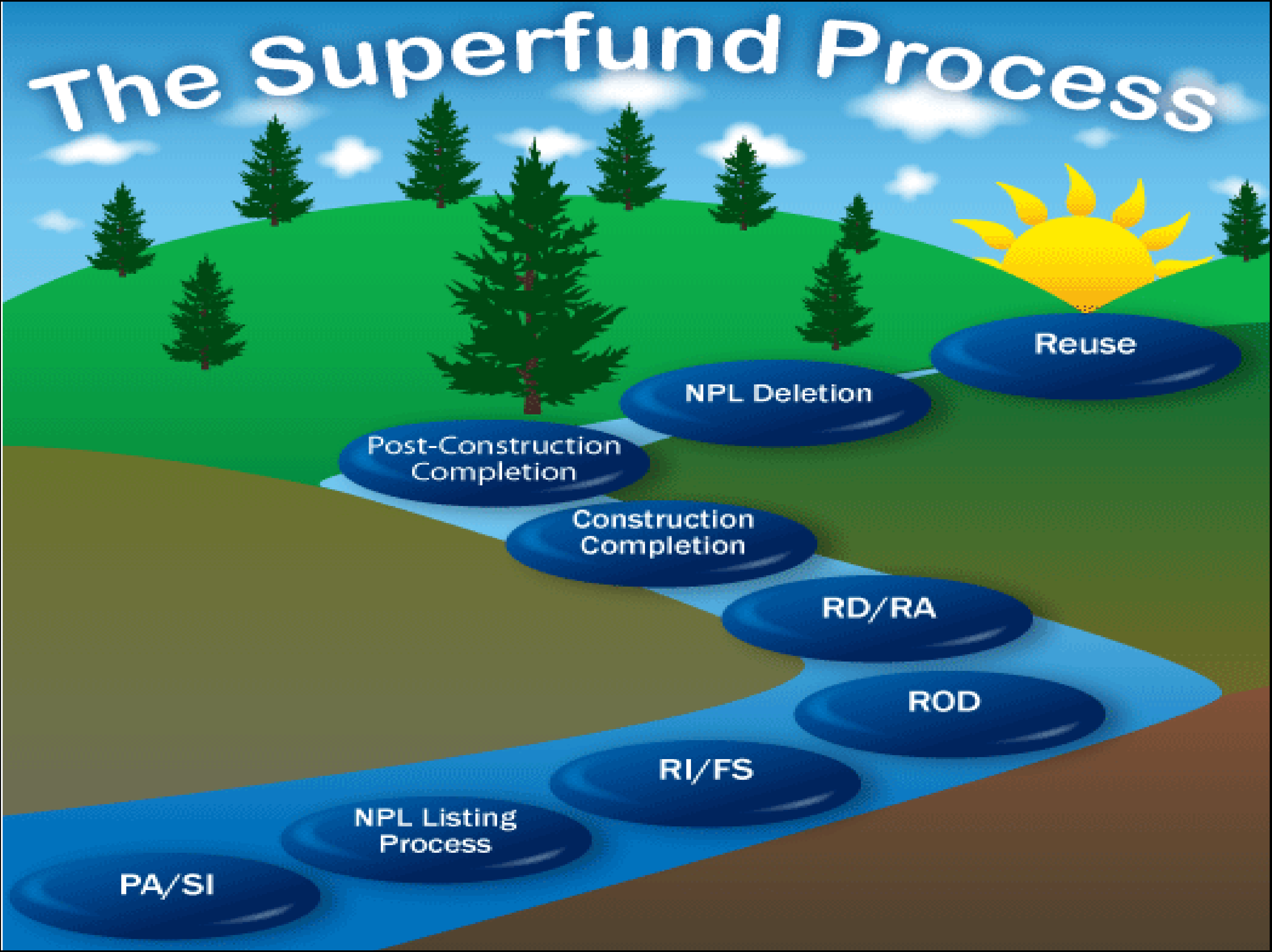
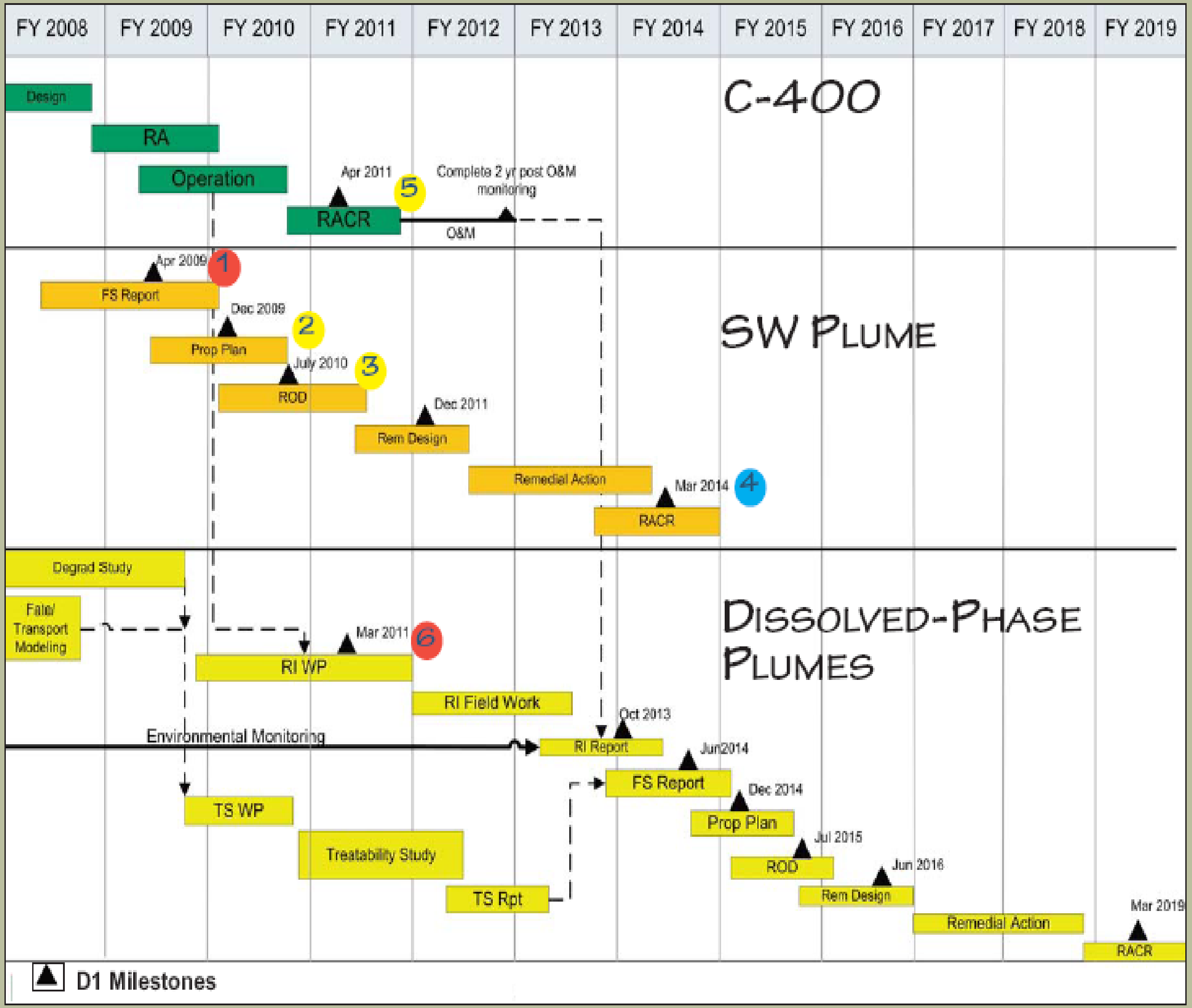
PGDP Site Regulatory Project Considerations


The Superfund Process
Reuse
NPL Deletion
Post-Construction Completion
Construction Completion
RD/RA
ROD
RI/FS
NPL Listing Process
PA/SI

Groundwater Operable Unit Schedule

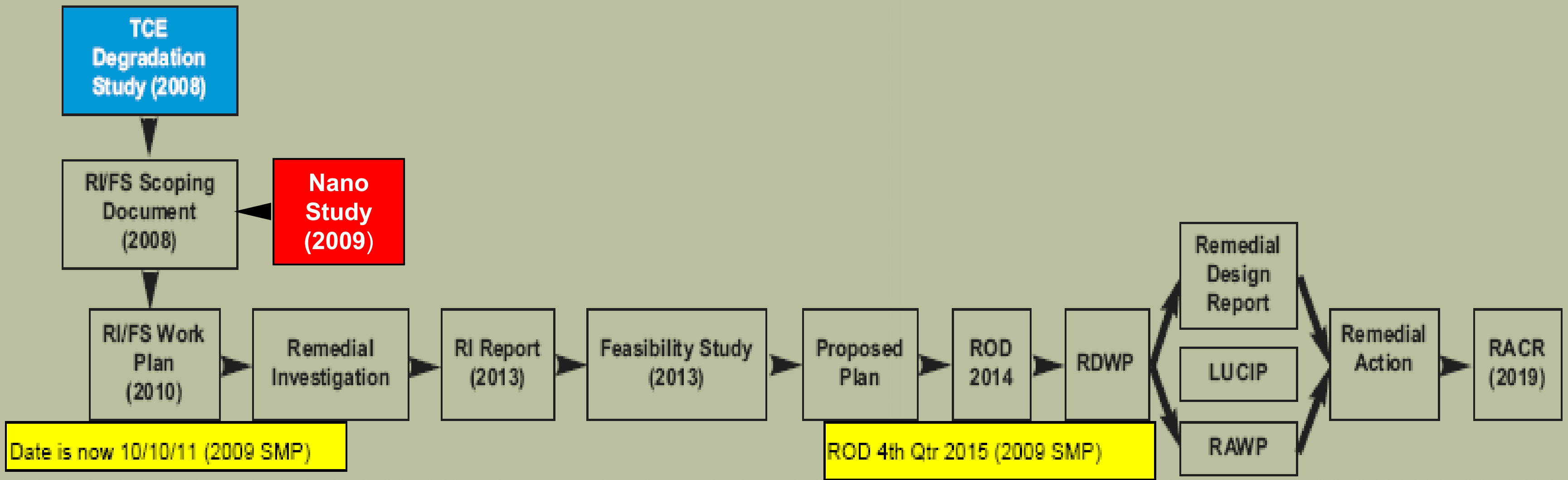


SMP Milestones

1. SW Plume FFS - 7/28/09
2. SW Plume Proposed Plan — 3/25/10
3. SW Plume ROD — 9/17/10
4. SW Plume Remedial Action Completion Report — 6/28/15
5. C-400 Remedial Action Completion Report — 4/26/2011
6. Dissolved-Phase Plume RI/FS Work Plan — 3/10/11 (planning date)

- Yellow: FY-07 SMP Approved Enforceable Milestone included in FY-08 SMP
- Red: FY-08 SMP Proposed New Milestone
- Blue: Out-year milestone proposed for evaluation/modification in FY09 SMP

Dissolved Phase Plume Schedule Overview and Status



Near-Term 2006 - 2009

- Support TCE Fate & Transport analysis by performing necessary fieldwork and analysis as identified by Fate & Transport Working Group
- Update groundwater model
- Develop and submit to regulators RI/FS Scoping Document

Out-Year 2010-2019

- Development and regulatory approval of RI/FS Work Plan
- Implement RI fieldwork
- Development and regulatory approval of RI Report
- FS development and regulatory approval
- Development and regulatory approval of Proposed Plan
- Development and regulatory approval of ROD and LUCIP
- Development and regulatory approval of Remedial Design Work Plan
- Development and regulatory approval of Remedial Design Report and Remedial Action Work Plan
- Implement remedial action
- Development and regulatory approval of Remedial Action Completion Report

PGDP Site Regulatory Project Considerations

Identification of all Federal and State ARAR's that address the injection of substances into ground/groundwater for purposes of remediation

TS Workplan Template

(from Iron Filings TS)

Example Work Plan

- **EXECUTIVE SUMMARY**

- **1.0 INTRODUCTION**
  - **1.1 BACKGROUND INFORMATION**
    - 1.1.1 Project Description
    - 1.1.2 Background Information
      - Location
      - Demography and Land Use
      - Climate
      - General History
  - **1.2 REGULATORY COMPLIANCE**
    - 1.2.1 Location Specific ARARs
    - 1.2.2 Chemical Specific ARARs
    - 1.2.3 Action-specific ARARs

- **2.0 TREATABILITY STUDY GOAL AND OBJECTIVES**
  - **2.1 TREATABILITY STUDY GOAL**
  - **2.2 TREATABILITY STUDY OBJECTIVES**
  - **2.3 DATA QUALITY OBJECTIVES**
    - 2.3.1 Intended uses of Acquired Data
    - 2.3.2 Intended Users of Data
    - 2.3.3 Analytical Quality Levels and Quality Control Levels

Example Work Plan

- **3.0 DESCRIPTION OF TREATMENT TECHNOLOGY**
  - **3.1 BACKGROUND**
  - **3.2 DESCRIPTION OF TECHNOLOGY**
  - **3.3 REVIEW OF LITERATURE**
    - 3.3.1 Degradation of Trichloroethylene
      - Overview of research
      - Summary of findings
    - 3.3.2 Precipitation of Technetium-99

- **4.0 EXPERIMENTALL APPROACH/DESIGN**
  - **4.1 EXPERIMENTAL APPROACH**
    - 4.1.1 Tier I: Evaluate Iron Sources
    - 4.1.2 Tier II: Optimize Process Variables
    - 4.1.3 Tier III: Assess Long-term Performance
  - **4.2 VARIABLES AFFECTING PERFORMANCE**

Example Work Plan

- **5.0 EQUIPMENT DESIGN AND EXPERIMMENTAL PROCEDURES**
  - **5.1 DESIGN CRITERIA**
  - **5.2 PROCEDSS DESCRIPTION**
  - **5.3 EQUIPMENT DESCRIPTION**
    - 5.3.1 Bag Filter (G-004)
    - 5.3.2 Flow Control Valves
    - 5.3.3 Static Mixers (L-011 and L-002)
    - 5.3.4 Iron Filings Reactor Vessel and Reactive Media
    - 5.3.5 Acid Feed System
    - 5.3.6 Reducing Agent Feed System
    - 5.3.7 Instruments and Controls
    - 5.3.8 Piping, Valves, and Fittings
    - 5.3.9 Equipment Support Skid
  - **5.4 OPERATION AND MAINTENANCE REQUIREMENTS**
    - **5.4.1** Process Operation and Control
    - 5.4.2 System Maintenance

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Example Work Plan

- **5.5 EXPERIMENTAL PROCEDURES**
  - 5.5.1 Pretest Setup and Testing
  - 5.5.2 Tier 1 Testing
  - 5.5.3 Tier II Testing
  - 5.5.4 Tier III Testing
- **5.6 SAMPLING AND ANALYSIS**
- **5.7 DATA MANAGEMENT**
- **5.8 DATA REPORTING**
- **5.9 WASTE MANAGEMENT PLAN**
  - 5.9.1 References
  - 5.9.2 Definitions
  - 5.9.3 General Waste Classification and Management Procedures
  - 5.9.4 Waste Streams
  - 5.9.5 Spill Containment
  - 5.9.6 Waste Handling and Segregation
  - 5.9.7 Packaging and Marking
  - 5.9.8 Storage, Transportation, and Transfer
  - 5.9.9 Waste Classification Requirements

Example Work Plan

- **REFERENCES**
-
- **APPENDIX A: TREATABILITY STUDY SAMPLING AND ANALYSIS PLAN FOR THE Fe/Pd NANO PARTICLE TREATMENT STUDY, NORTHWEST PLUME INTERIM REMEDIAL ACTION, PADUCAH GASEOUS DIFFUSION PLANT, PADUCAH, KENTUCKY**
- **APPENDIX B: MAINTENANCE SHEETS**
- **APPENDIX C: EXAMPLE LOG SHEETS FOR TREATABILITY STUDY TESTS**
- **APPENDIX D: HEALTH AND SAFETY PLAN ADDENDUM**
- **APPENDIX E: WASTE DISPOSAL FORMS AND LOGS**

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Technical Issues
to be addressed by Treatability Study

1. Delivery capabilities for nanoparticle introduction (in-situ)
   a. Method
   b. Optimization of delivery
2. Performance at site RGA temps – (60^{o} F avg. vs. 70^{o} F)
3. Performance at site groundwater velocities (1 – 3 ft/day vs 12 – 83 ft/day)
4. Reactivity of nanoparticles in-situ
   a. TCE
   b. Tc-99
5. Spatial reactivity limits relative to
   a. TCE concentration
   b. Matrix interaction
   c. Geochemical effects

Technical Issues to be addressed by Treatability Study

6. Fate of nano particles
    a. Chemical form of Fe
    b. Chemical form of dopant
    c. Geochemical stability of Fe
    d. Geochemical stability of dopant
    e. Concentration changes relative to CWA constituents
7. Bimetallic nanoparticles & Tc-99
    a. Fate
        i. precipitate
        ii. matrix
    b. Chemical form
    c. Stability
8. General Implementability
9. Data Quality
10. Costs

Technical Issues to be addressed by Treatability Study

How will TS Workplan Address these issues?

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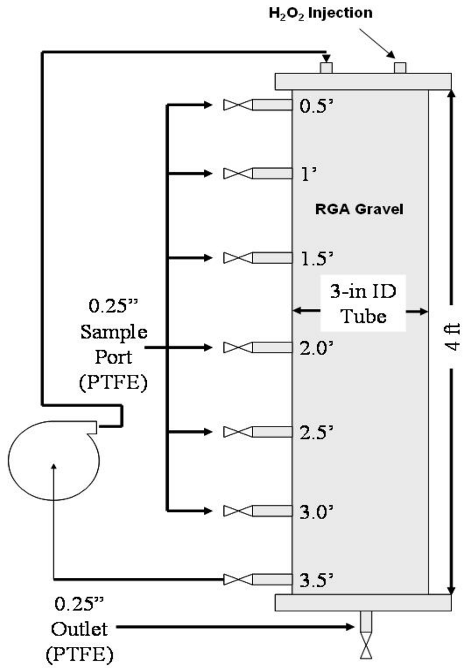
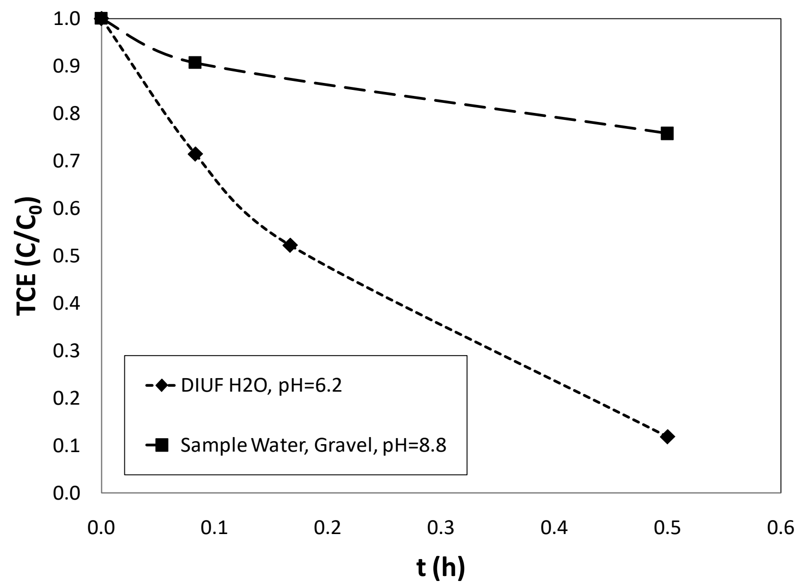
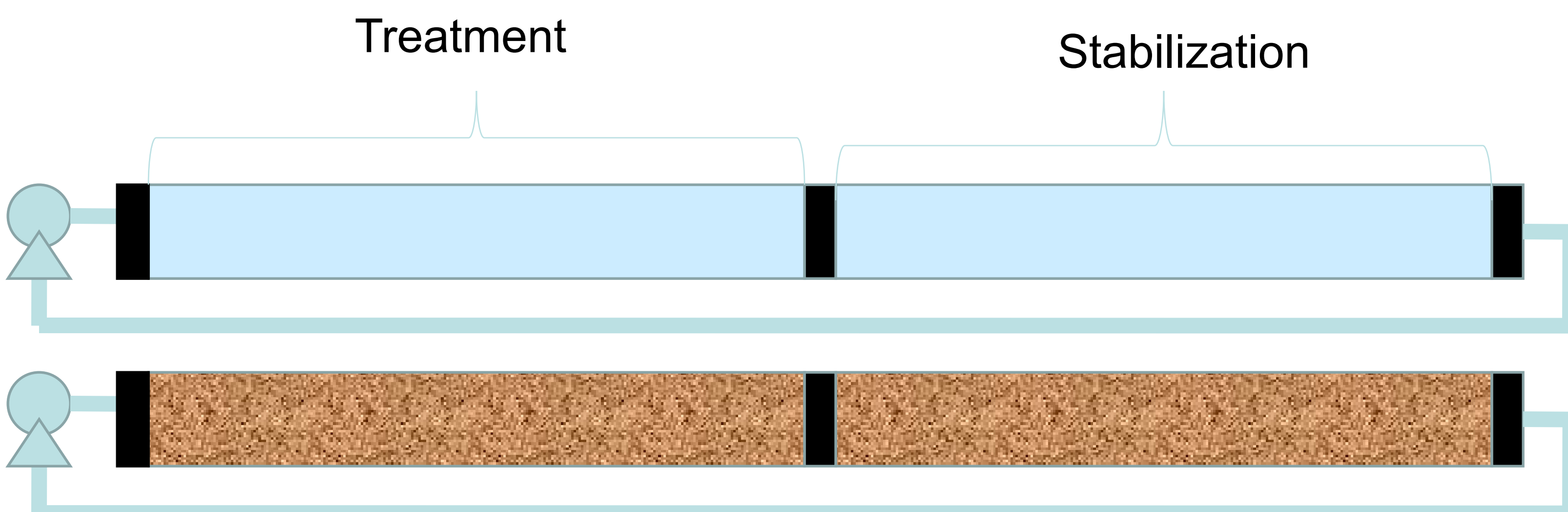
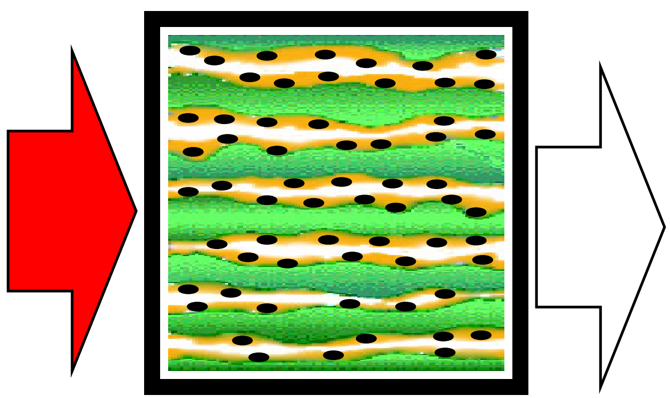
Laboratory/Bench Experiments

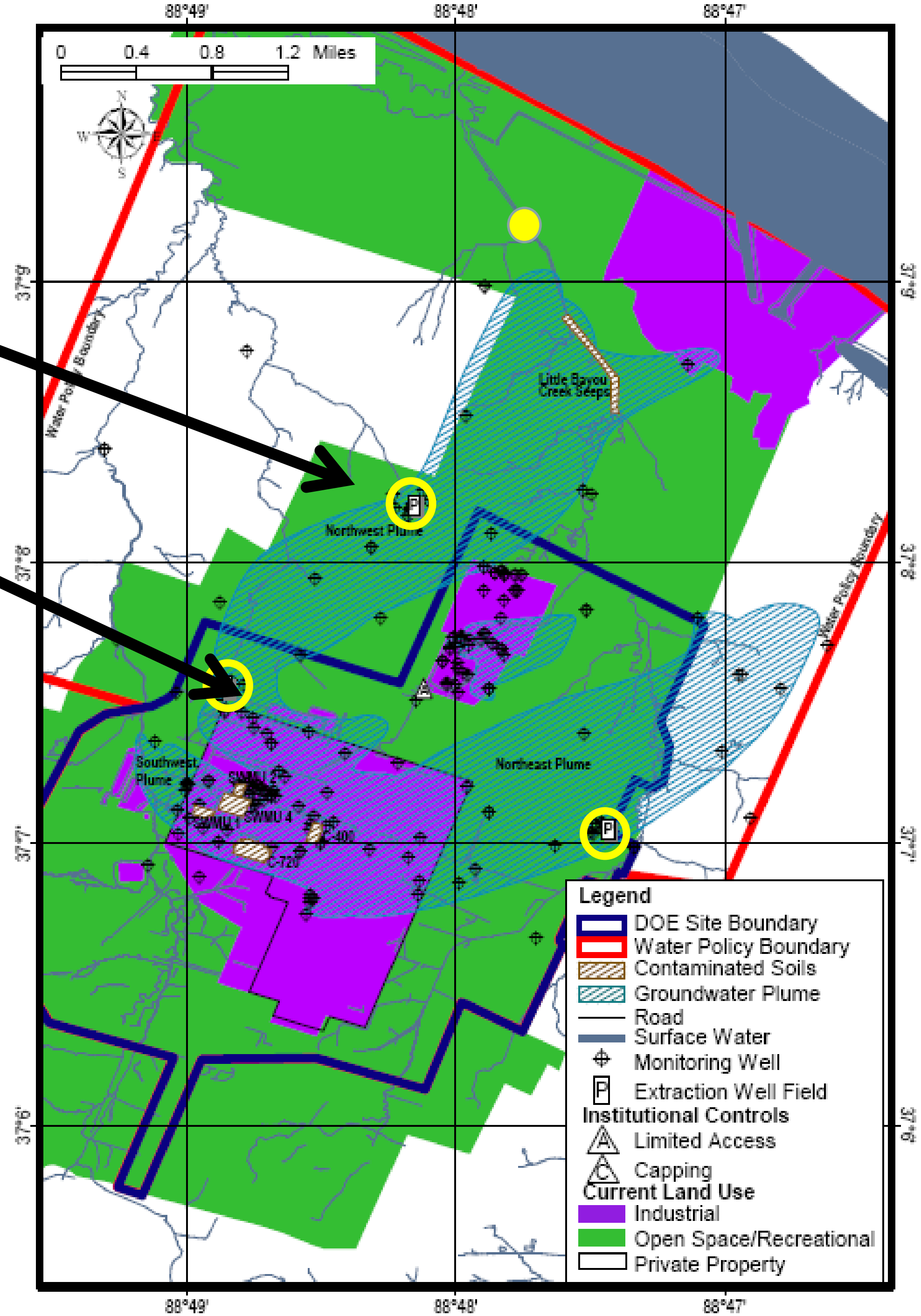




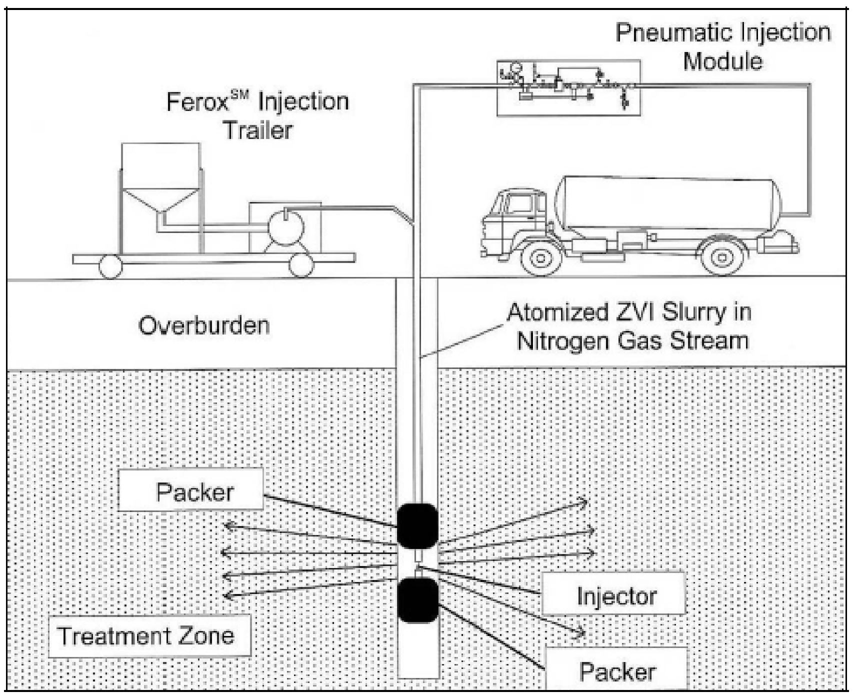


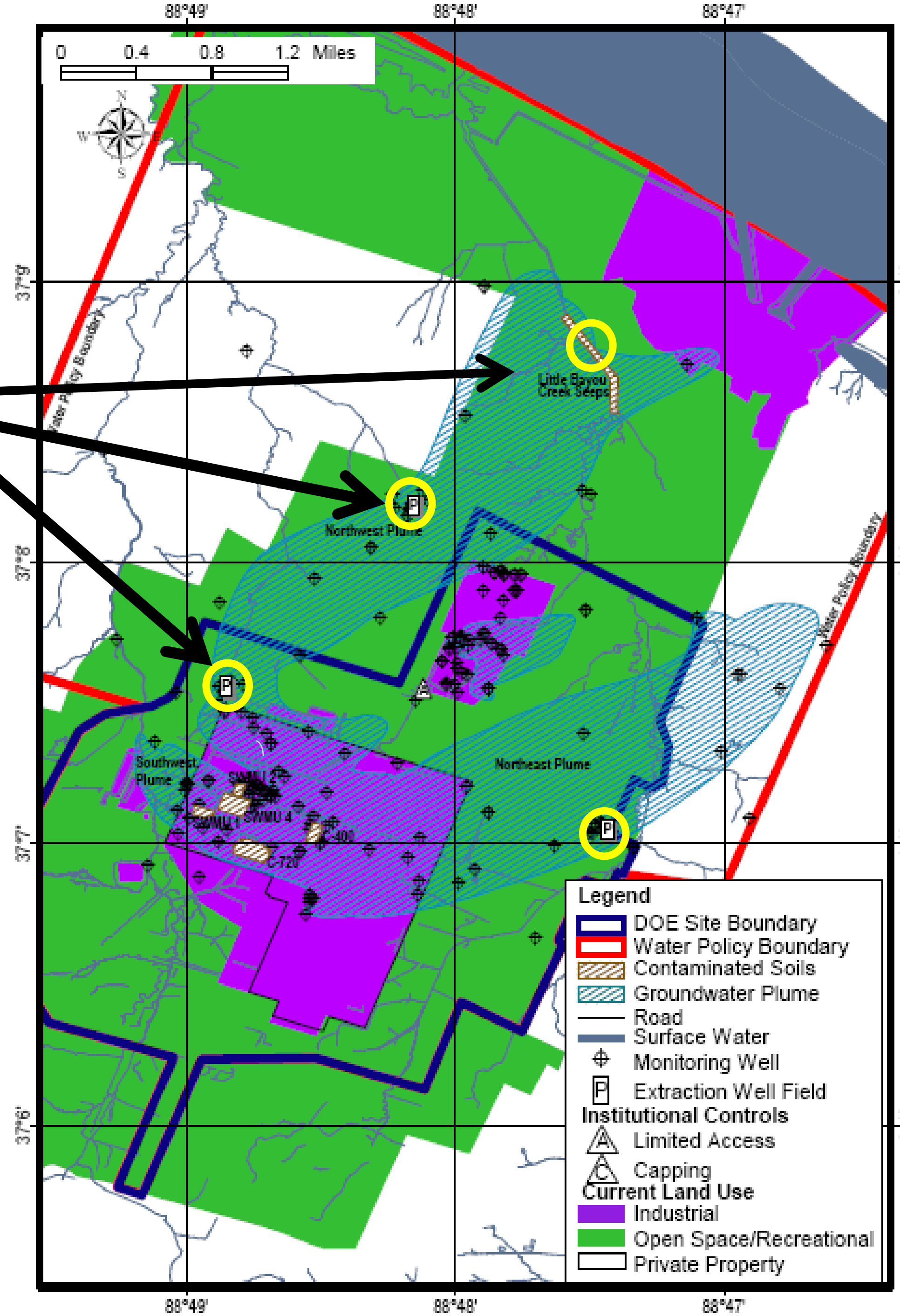
Perform Ex-situ Experiments at P&T site



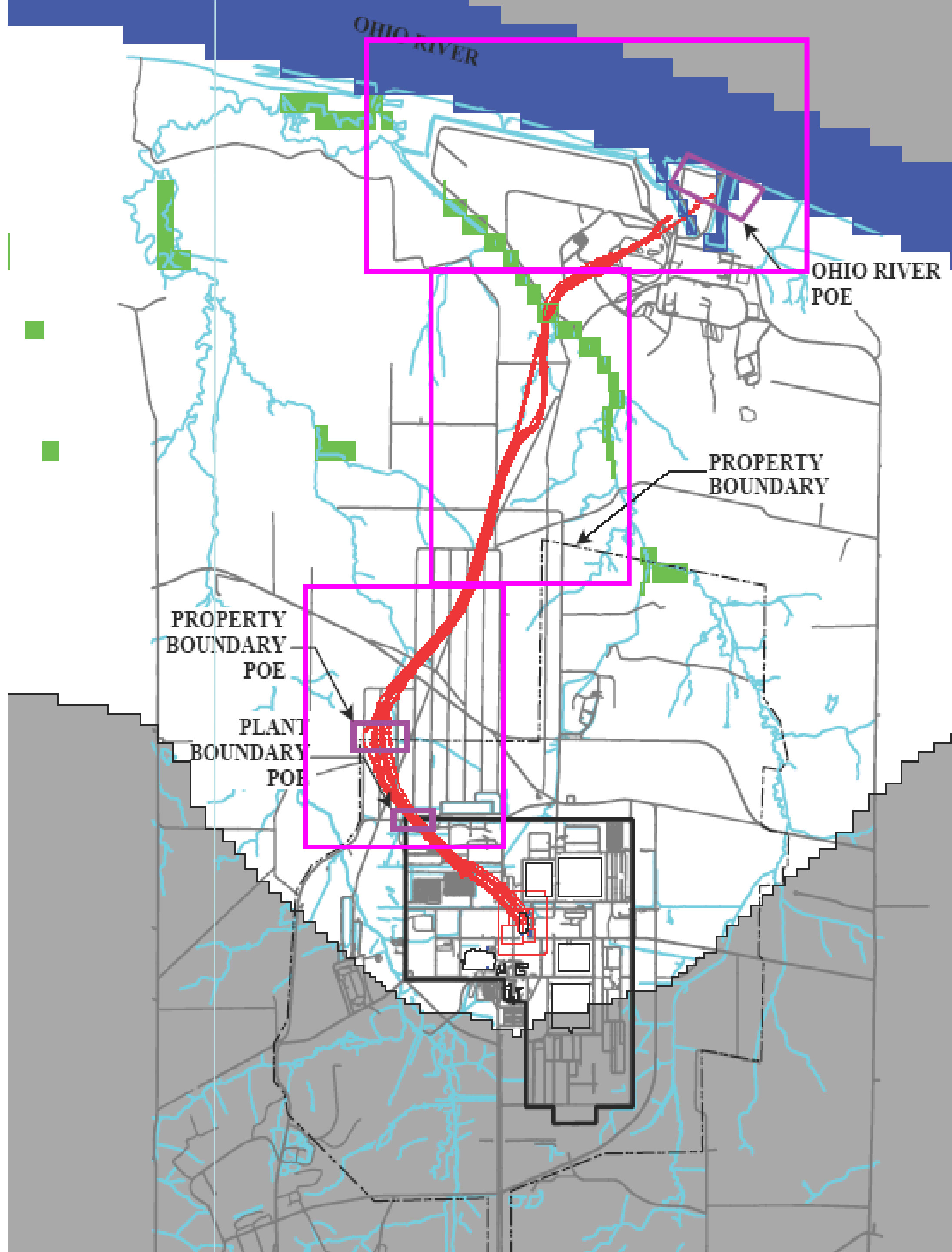


Perform In-Situ Experiments

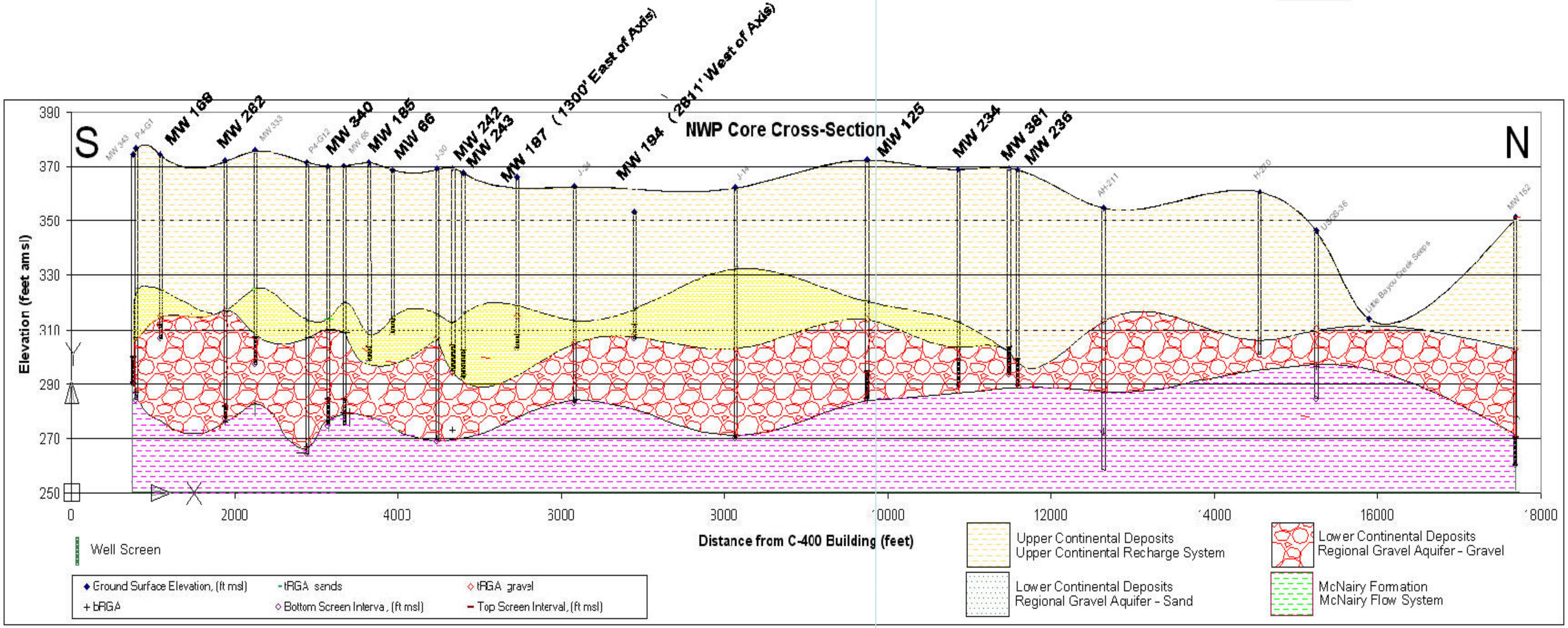




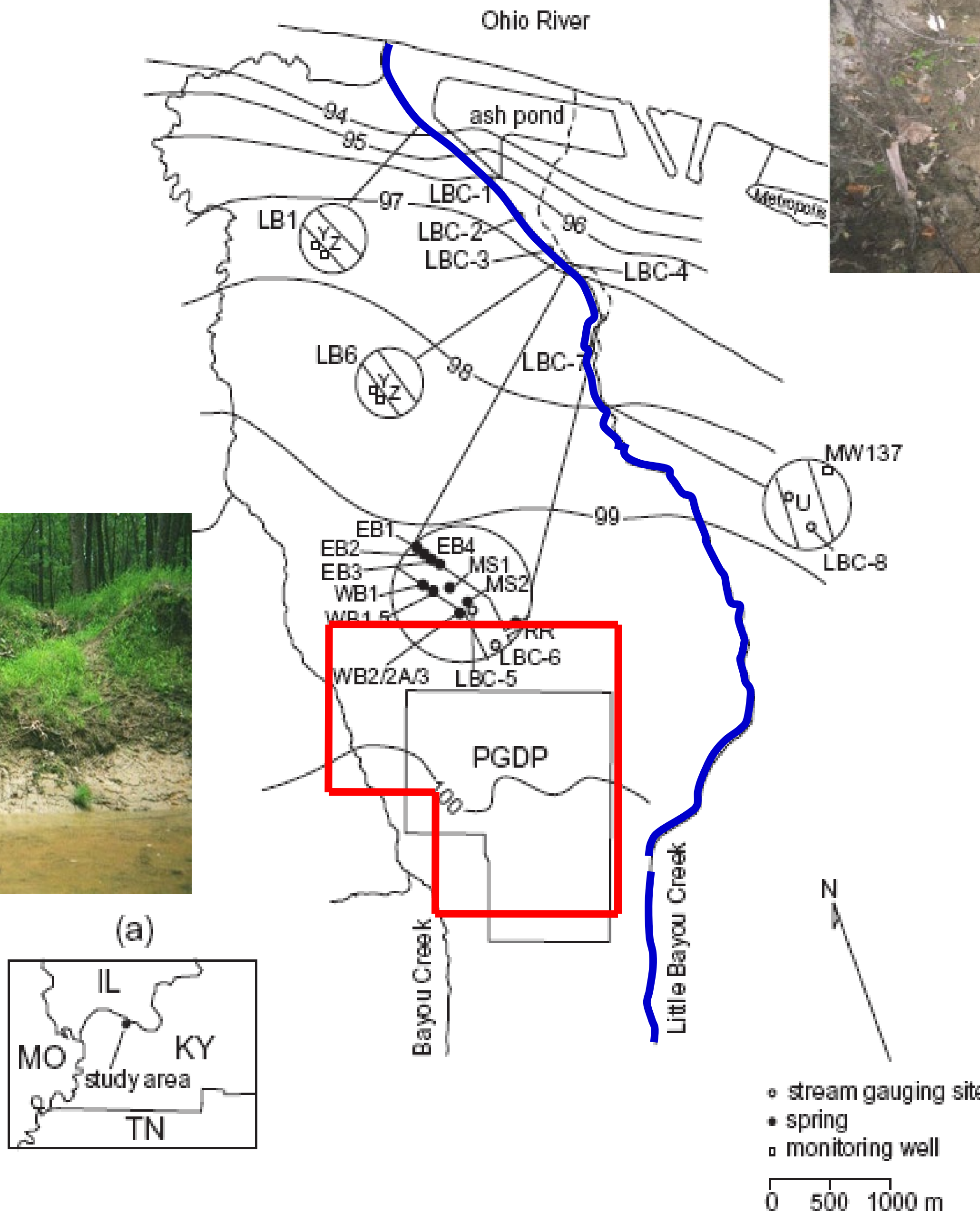
Characterize Aquifer Flow Path



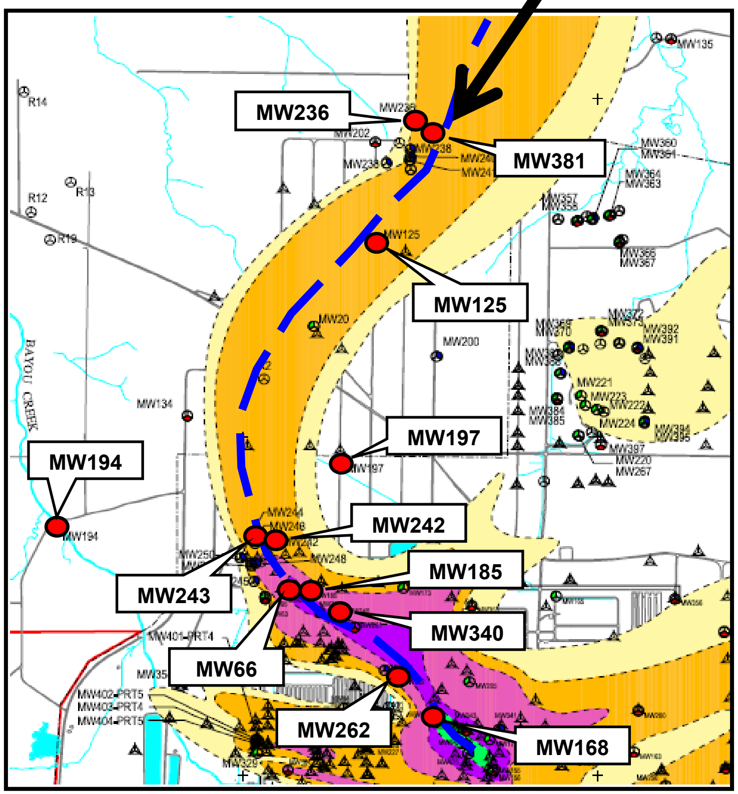
Characterize Aquifer Geology

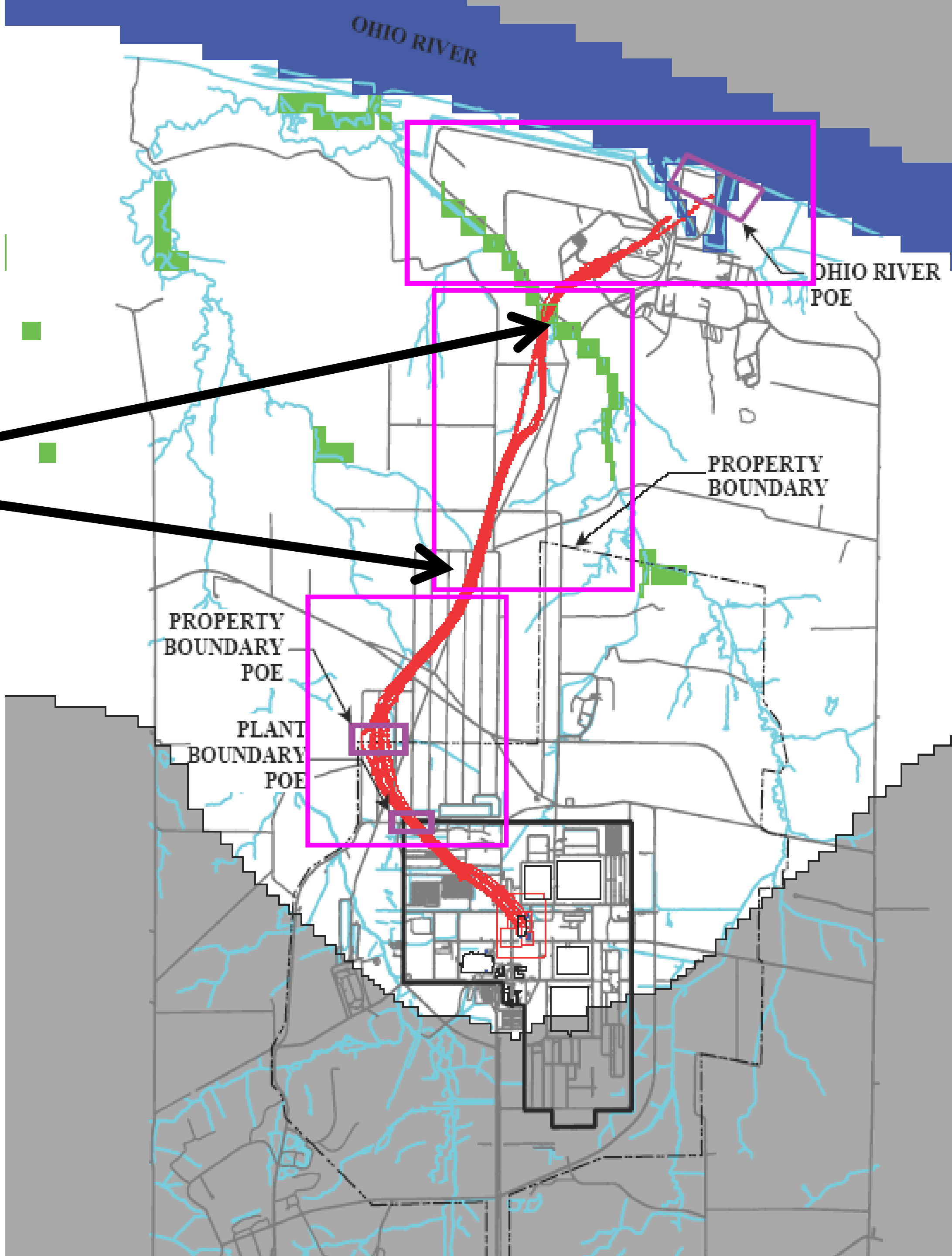


Characterize Seeps



Perform Tracer Study to Confirm Flow Path(s)





Characterize Aquifer Chemistry

Table C.18. Surveillance Geochemical Wells (35)
MW20
MW99
MW100
MW125
MW134
MW145
MW152
MW161
MW163
MW188
MW193
MW206
MW201
MW242
MW243
MW255
MW256
MW257
MW258
MW260
MW261
MW288
MW291
MW292
MW328
MW329
MW339
MW343
MW381
MW403 Port 3
MW404 Port 3
MW404 Port 4
MW404 Port 5
MW409
MW414

Table C.19. Surveillance Geochemical Annual Analytical Parameters

Che[...]	Metals (total and dissolved)*
Sulfate	Aluminum
Nitrate	Antimony
Total Organic Carbon	Barium
Chloride	Beryllium
Total Dissolved Solids	Cadmium
Silica	Calcium
Fluoride	Chromium
Phosphate	Cobalt
	Copper
Field Parameters	Iron
Barometric Pressure	Lead
Specific Conductance	Magnesium
Depth to water	Manganese
Dissolved Oxygen	Molybdenum
Eh	Nickel
pH	Potassium
Temperature	Silver
Turbidity	Sodium
Alkalinity	Zinc
Ferrous Iron	Arsenic
	Mercury
Volatiles	Selenium
Ethene	Uranium
Ethane	
Methane	**PCBs**
	PCB, Total
	PCB-1016
	PCB-1221
	PCB-1232
	PCB-1242
	PCB-1248
	PCB-1254
	PCB-1260
	PCB-1268