Sustained-Release Permanganate: Reactive Barriers for Green and Sustainable Remediation

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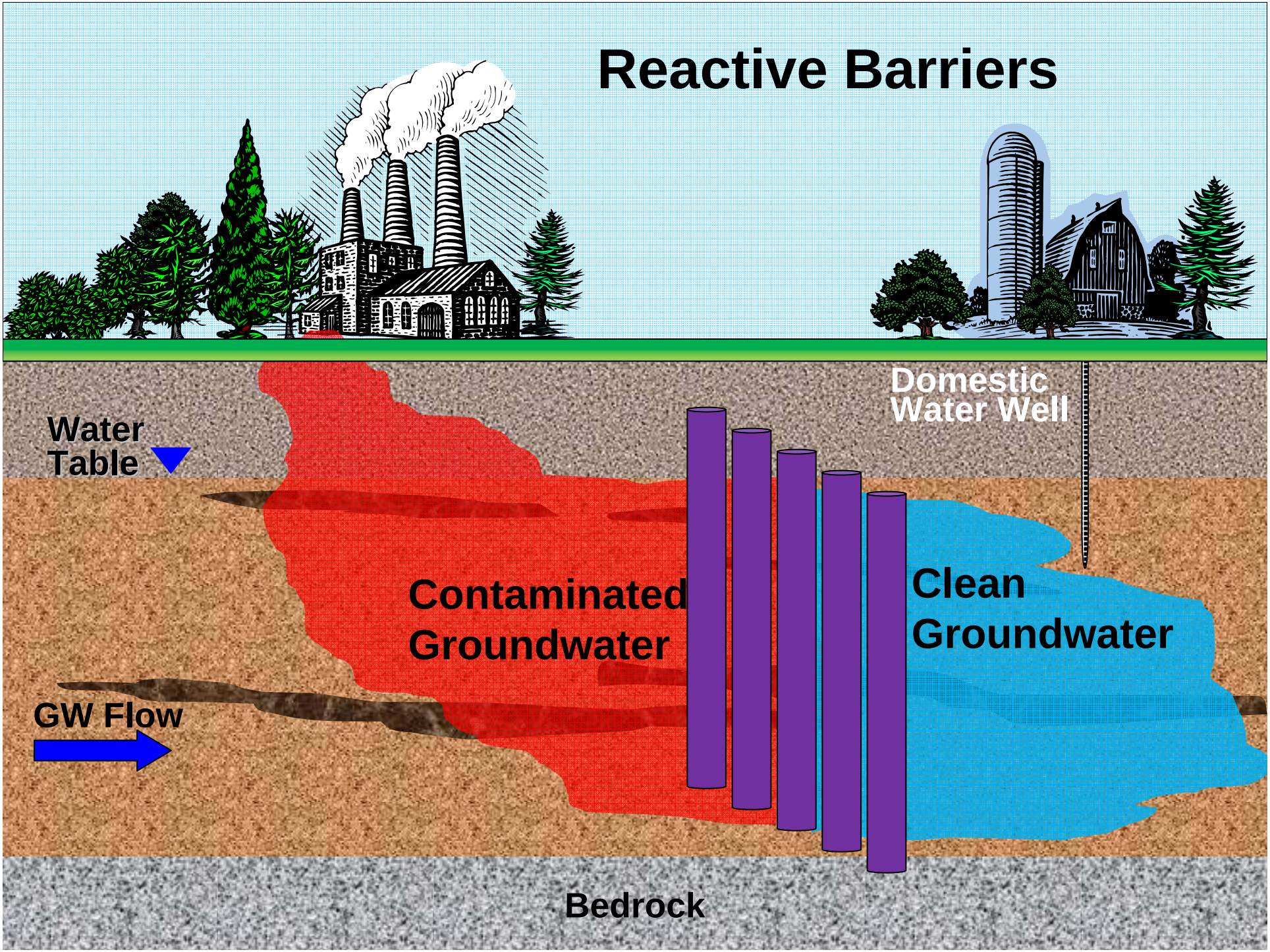
Agenda

- Background:
  - Permeable Reactive Barriers
- Technology Development :
  - Sustained-release permanganate
- Laboratory experiments (Carus)
- Field study (University of Nebraska)
- Next steps
- Questions

The Challenge

- All remedial technologies have an environmental impact...
  - Electricity/fossil fuel to power equipment
  - Aboveground treatment of extracted fluids
  - Landfill disposal
- Reactive materials have been used successfully to remove contaminants in soil and groundwater
  - Once emplaced, do not require continued supply of electrical/fossil fuel energies
  - Serve as long-term, low-cost passive treatment for destruction/transformation of toxic contaminants


Reactive Barriers
Domestic
Water Well
Water
Table
Contaminated
Groundwater
Clean
Groundwater
GW Flow
Bedrock

Technology Development – Sustained-Release Permanganate

- Promising lab and pilot-scale field studies investigating slow- release permanganate for barrier applications (e.g., Comfort et al. 2011; Dugan et al., 2011; Kang et al. 2004; Lee and Schwartz, 2007; Ross et al. 2005)

- 2003 Specialty Earth Sciences developed methods of encapsulation for sustained-release of reactants
  - *US Patent No. 7,431,849 B1 "Encapsulated Reactant and Process" (2008)*
  - *US Patent App. 12/169,434 "Encapsulated Reactant and Process" (2008)*
  - *US Patent App. 12/269,520 "A Process for Making Environmental Reactants" (2009)*

- *Carus holds exclusive licensing rights for manufacturing, sales, and distribution*

Technology Development – Sustained-Release Permanganate

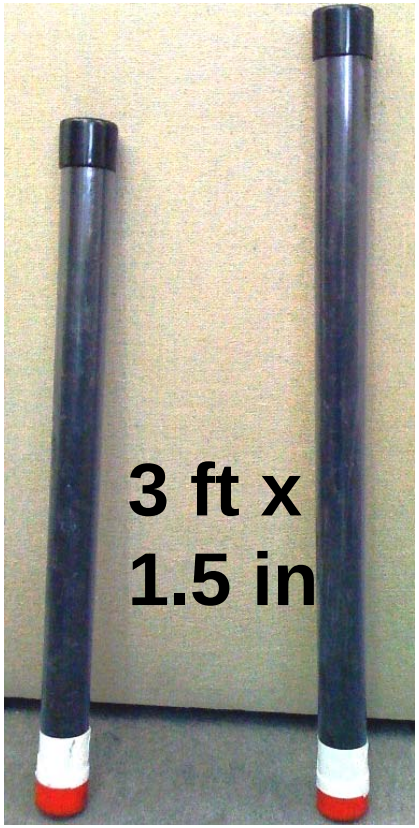
- RemOx® SR (Sustained-Released) is a potassium permanganate ($KMnO_4$)-based product dispersed in a solid paraffin wax matrix (60% to >80% $KMnO_4$)
- *This is the first oxidant-based reactive barrier technology for long-term passive treatment of chlorinated solvents*
- Potential for other reactants to be used (e.g., other oxidants, activators, catalysts, oxygen-release compounds, heavy metal immobilization amendments)

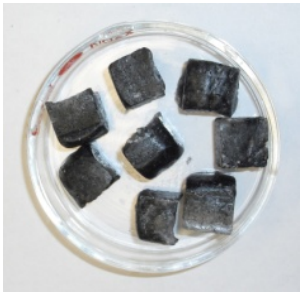
Technology Development – Sustained-Release Permanganate

- Paraffin wax matrix properties:
  - Stable and non-reactive with the oxidant
  - Isolates reactants from instant dissolution in groundwater
  - Nontoxic and biodegradable
  - Facilitates slow sustained release of reactant(s) over long periods of time (e.g., years)

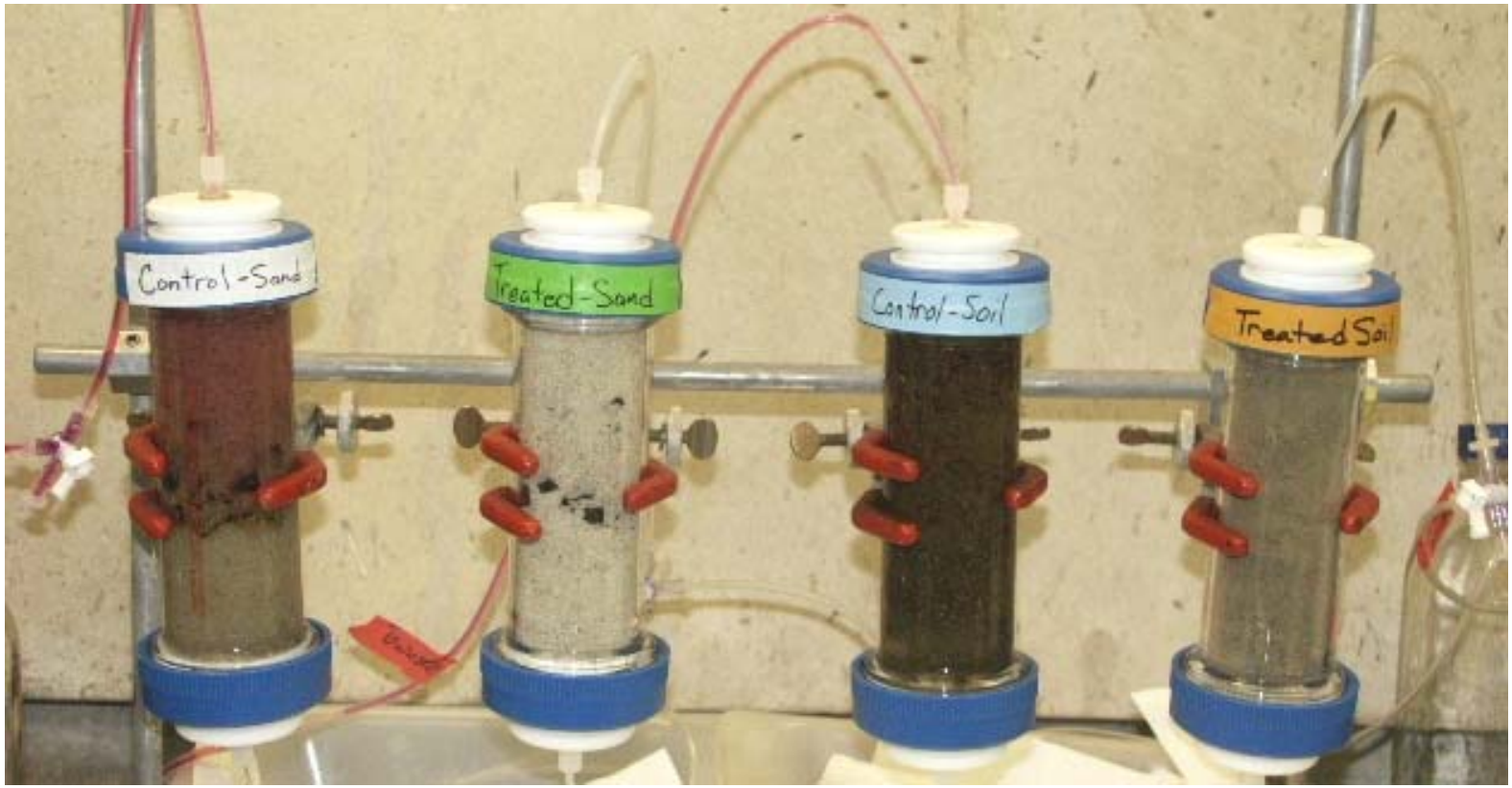
Technology Development – Sustained-Release Permanganate

- Solid product formed as candle, chipped for barrier applications or further processed for hydrofracturing into low permeability media





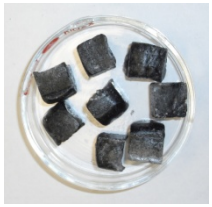
Experimental Approach – Sustained-Release Permanganate

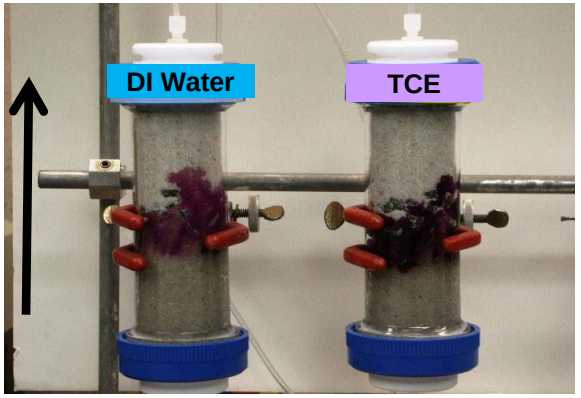


– Column experiments to evaluate permanganate release and treatment performance under dynamic flow conditions

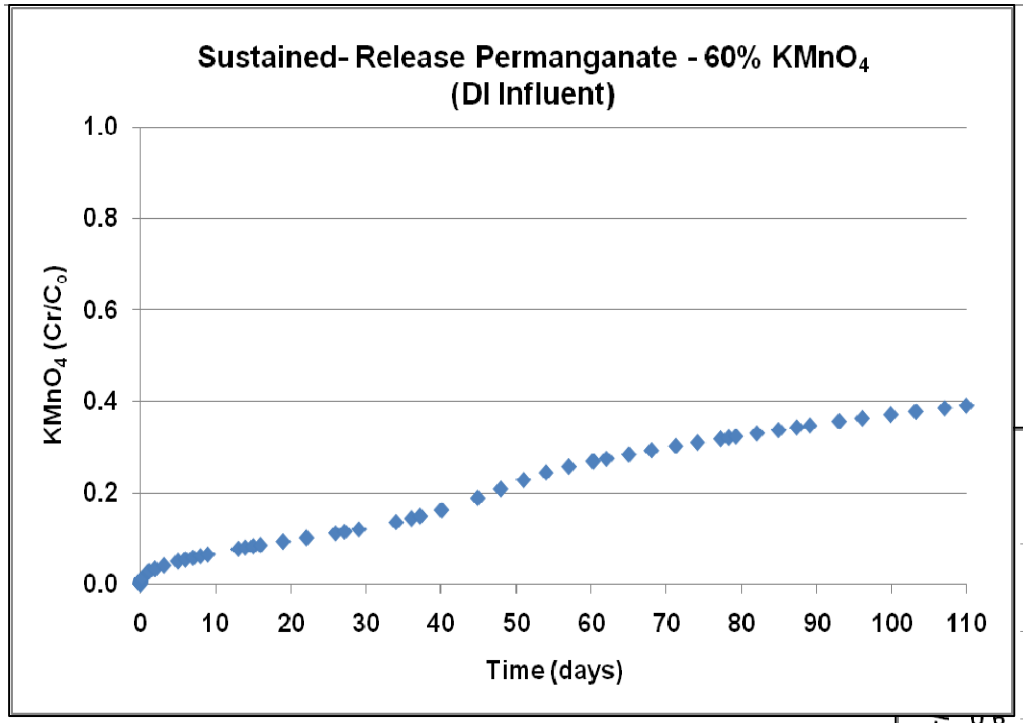
Methods

- Sand Columns (30 cm x 4.8 cm)
  - 20/30 mesh silica sand
  - 35 g SRP 60% mass loading (21 g $KMnO_4$)
  - DI water or dissolved TCE
  - Trichloroethene (TCE) influent ~ 0.7 mg/L
  - Flow rates (0.2 or 0.7 mL/min)
- $KMnO_4$ dissolves and diffuses from wax matrix to react and degrade TCE

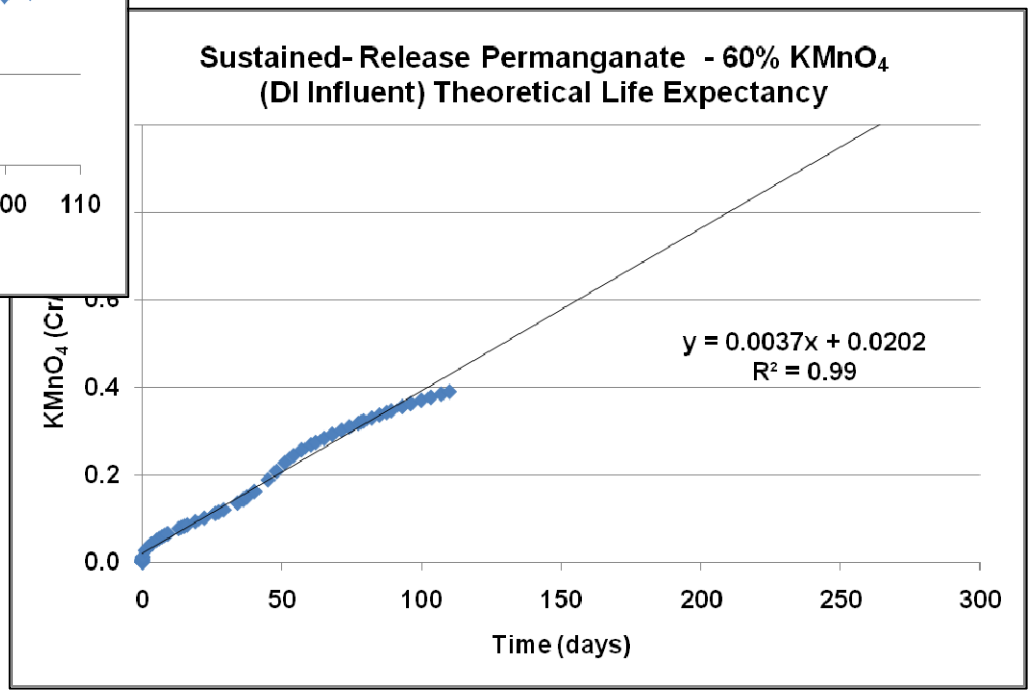




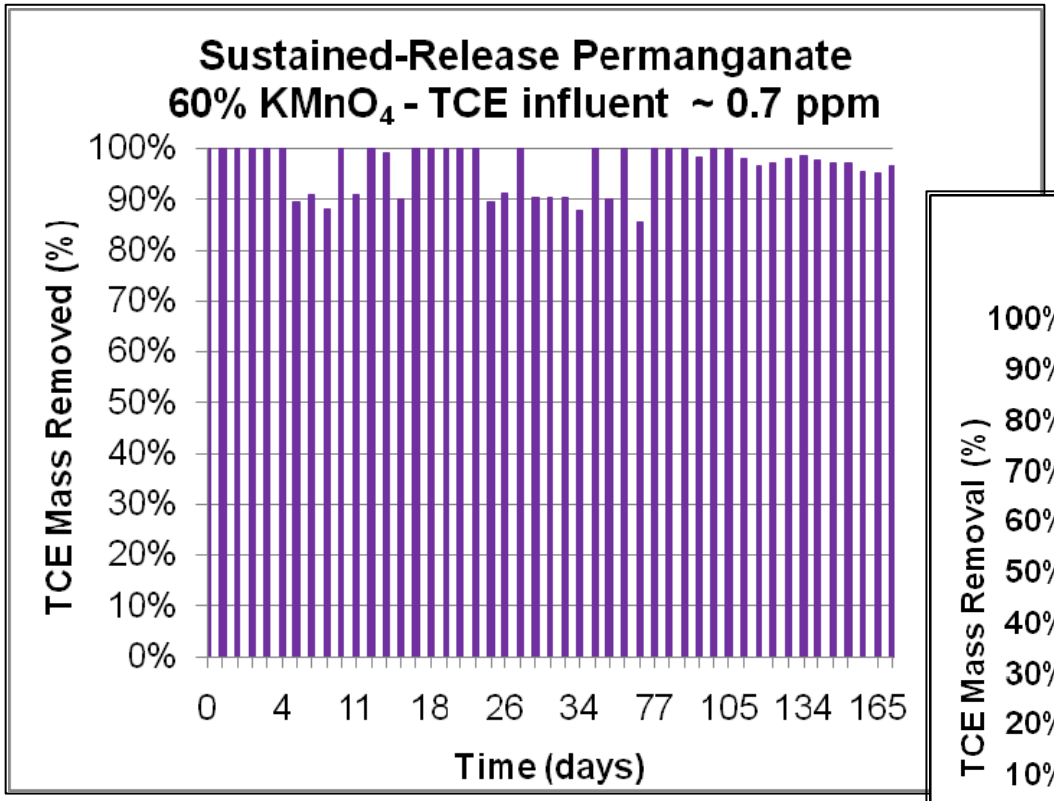
Results

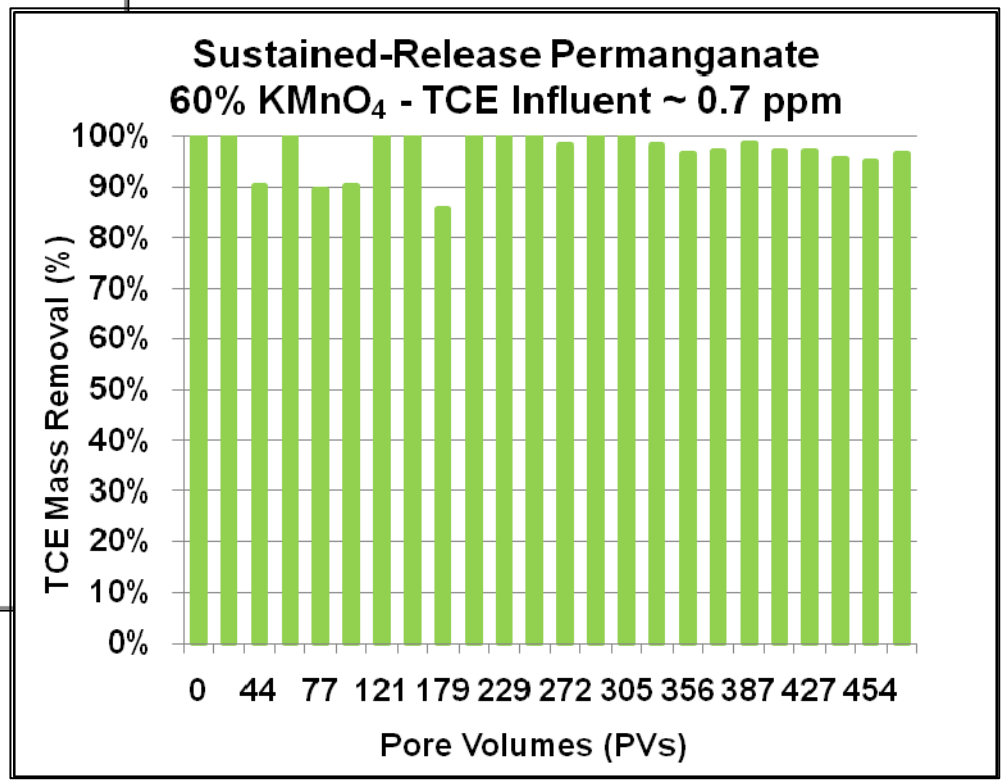


Theoretical SR life expectancy > 250 days



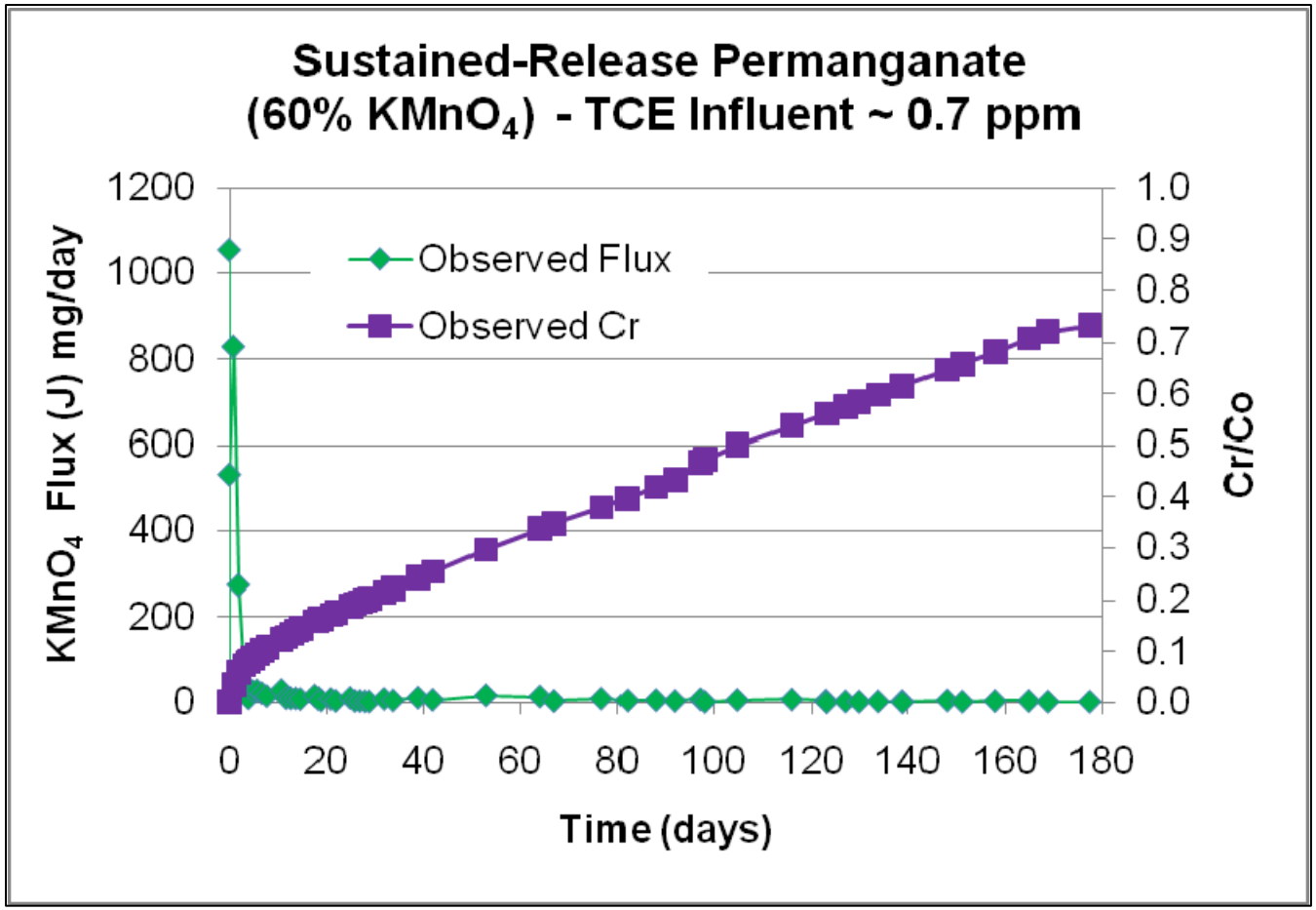
Results





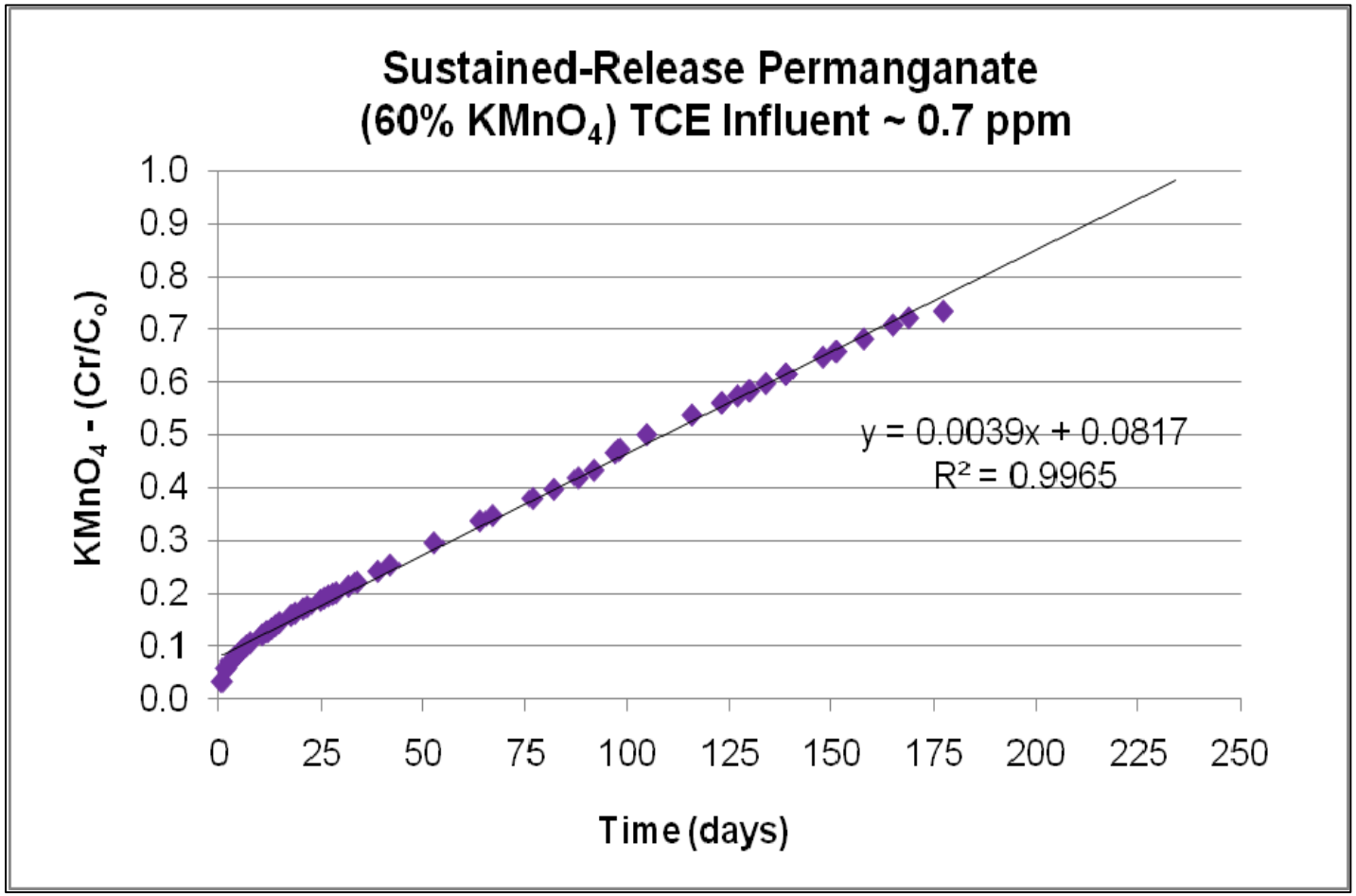
TCE mass removal 86% - 100% over 170 days or > 470 PVs

Results



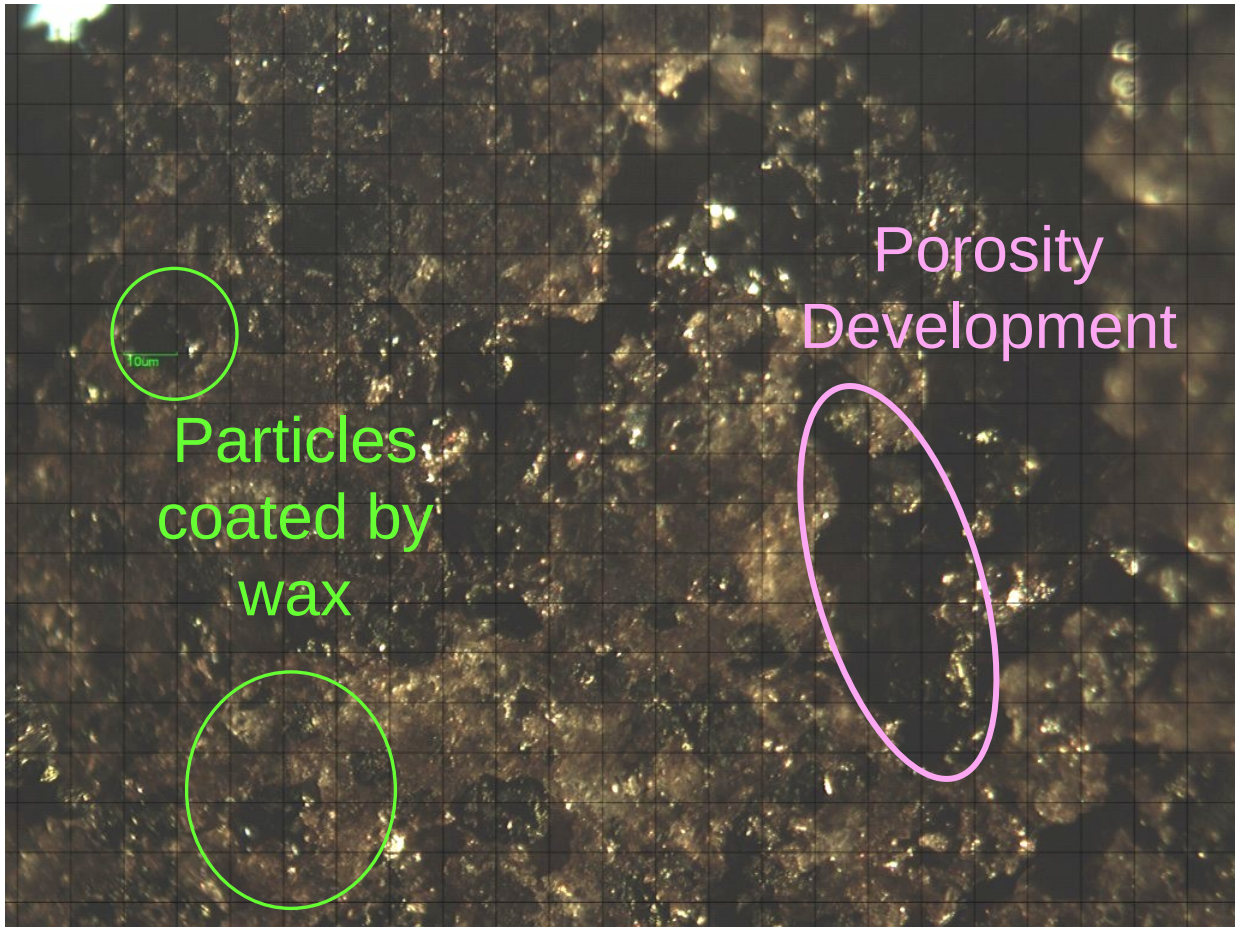
Average $KMnO_4$ conc. over last month = 240 ppm

Results



Theoretical SR life expectancy ~ 230 days

Results



~70% $KMnO_4$ reacted-released over 170 days..increased mass loading to enhance $KMnO_4$ utilization

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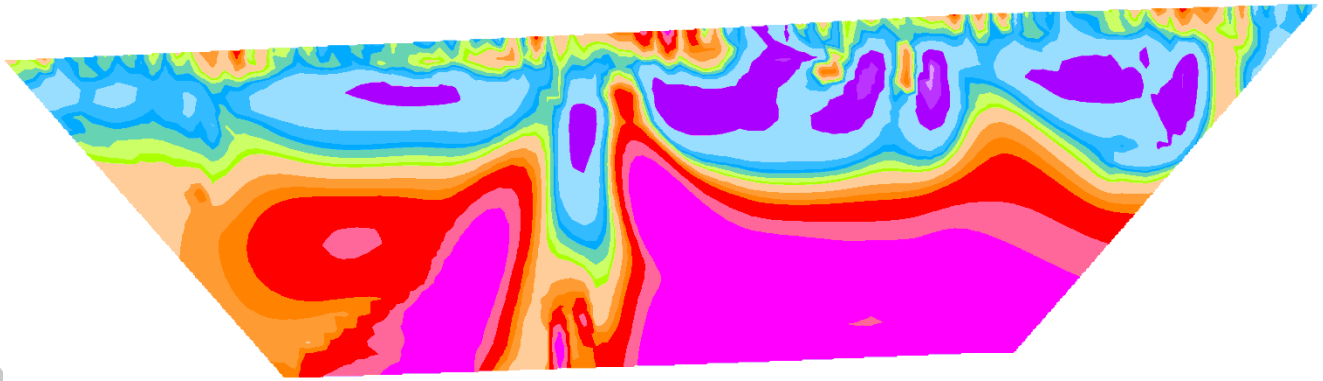
Cozad Former Solid Waste Disposal Site

University of Nebraska

Dr. Steve Comfort



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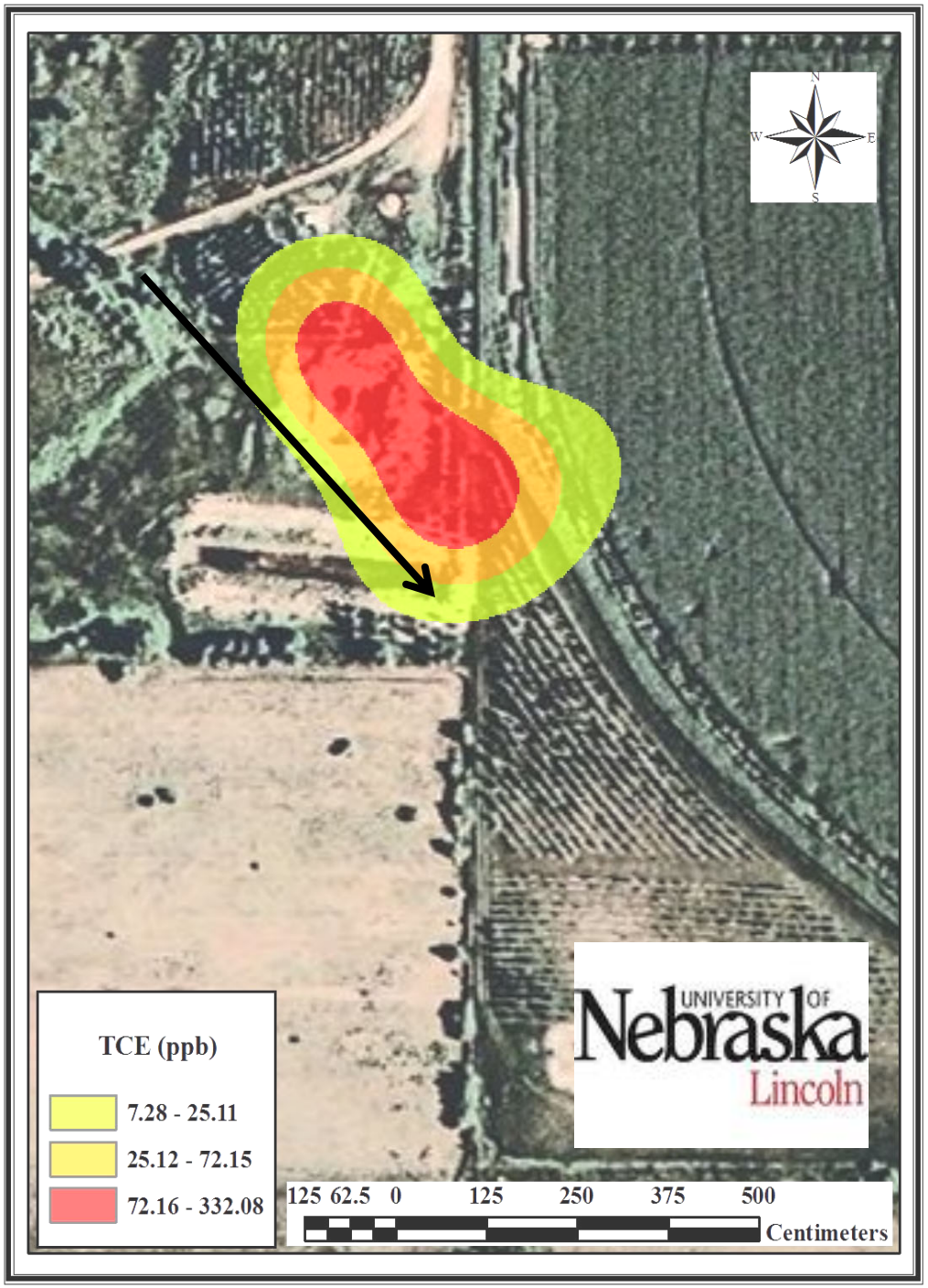
- Facility closed after TCE contamination found in underlying aquifer
- Majority of TCE in a low permeable silty-clay unit near surface of water table
- TCE (100-600 ppb)
- Darcy velocity = 0.045 in/day
- UNL with NDEQ wanted to implement low-cost passive system for TCE treatment in low permeability unit



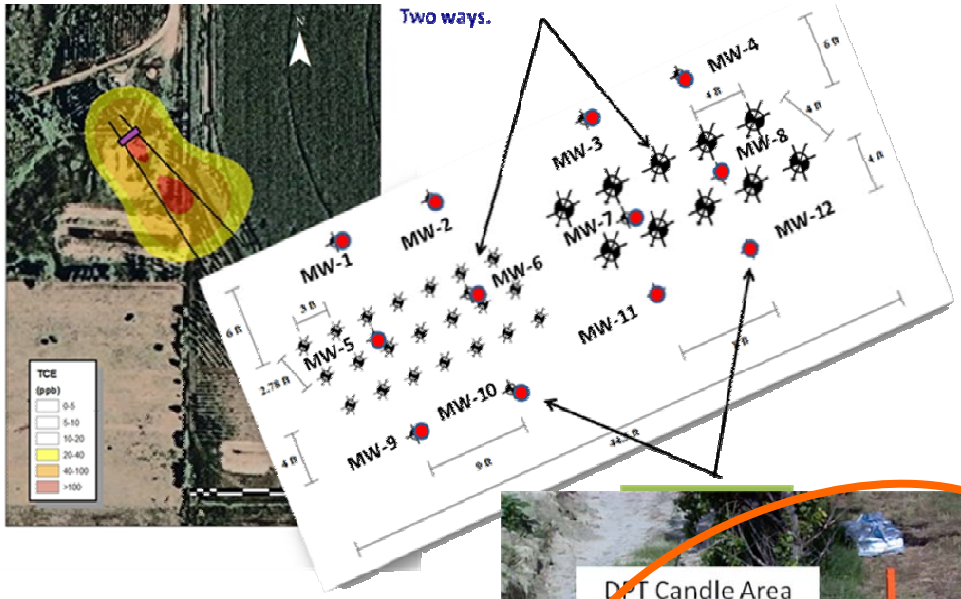
3-in well candles

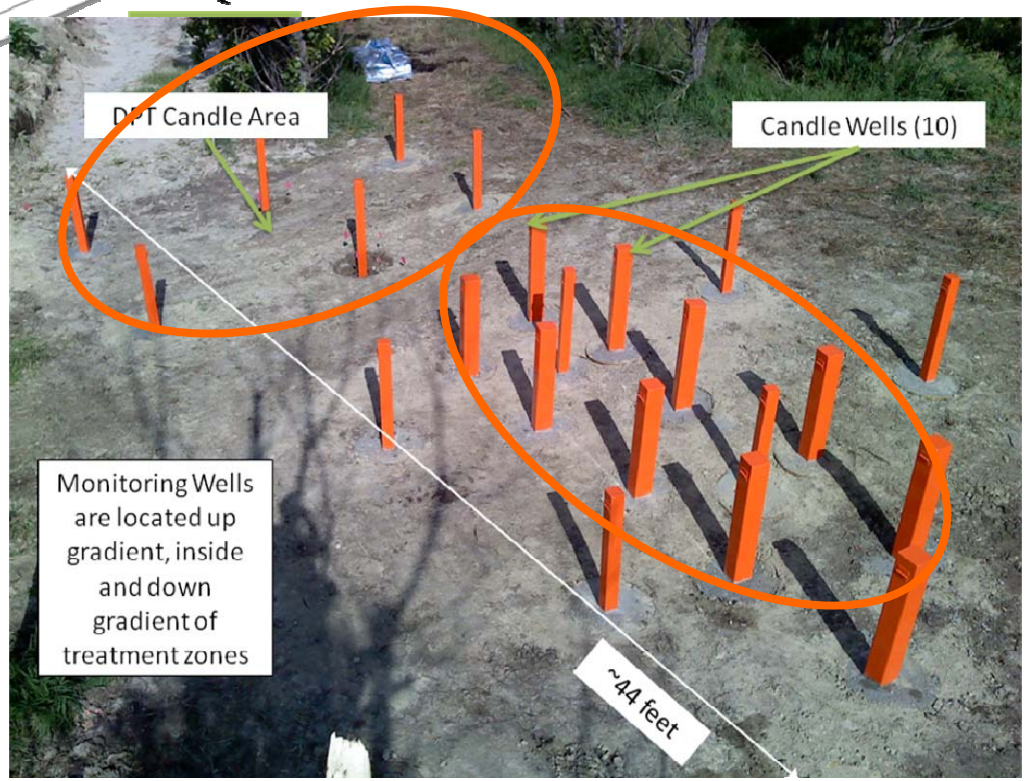
In situ candle holder & insertion tool to emplace SRPCs in 3-inch wells

2-in DPT candles

SRPC Reactive Barrier Installation

- 50 three inch injection well SRPCs
- 105 two inch DPT SRPCs





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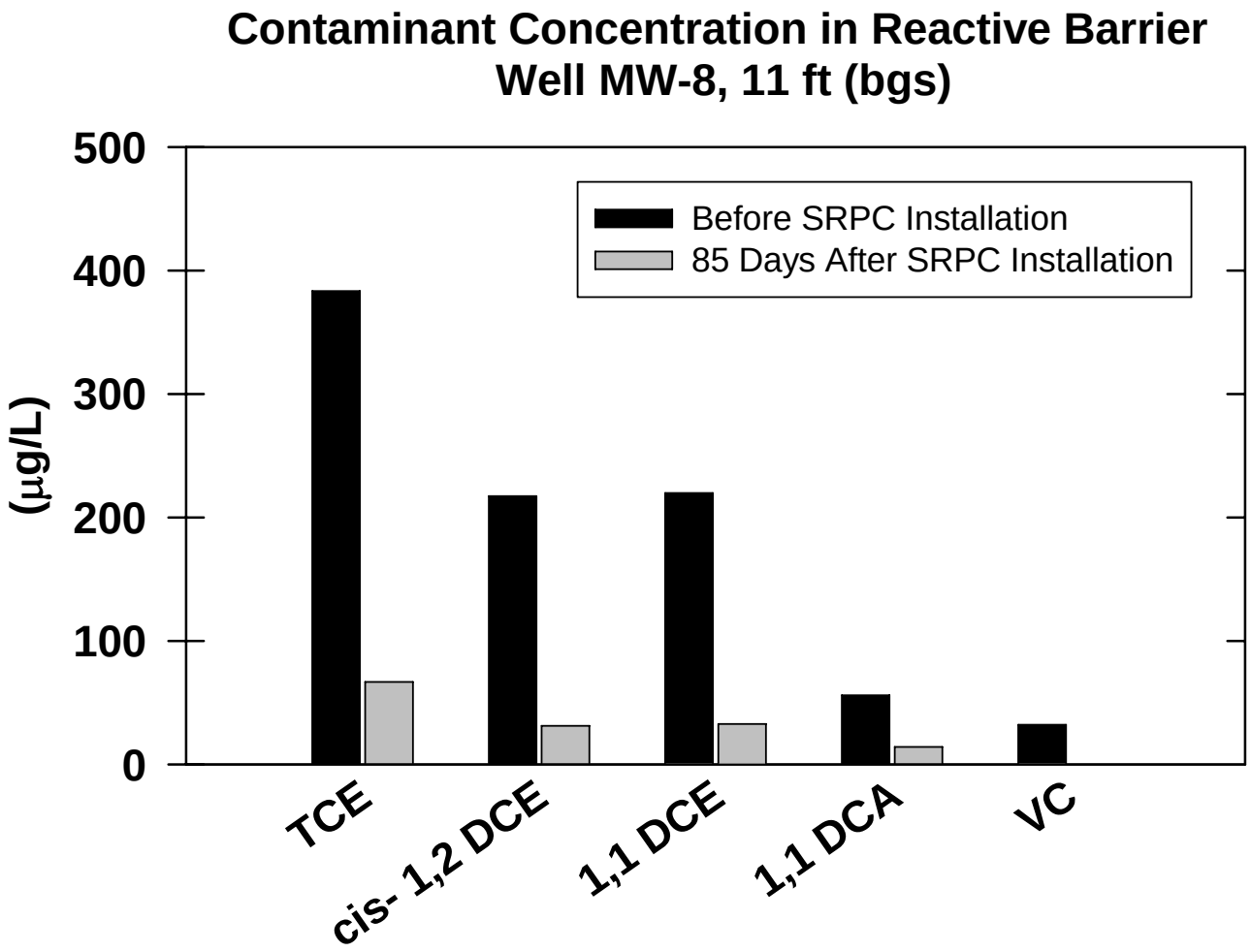
Results



- **Barrier installed June 2010**
- **After 85 days 64%-82% TCE reduction**

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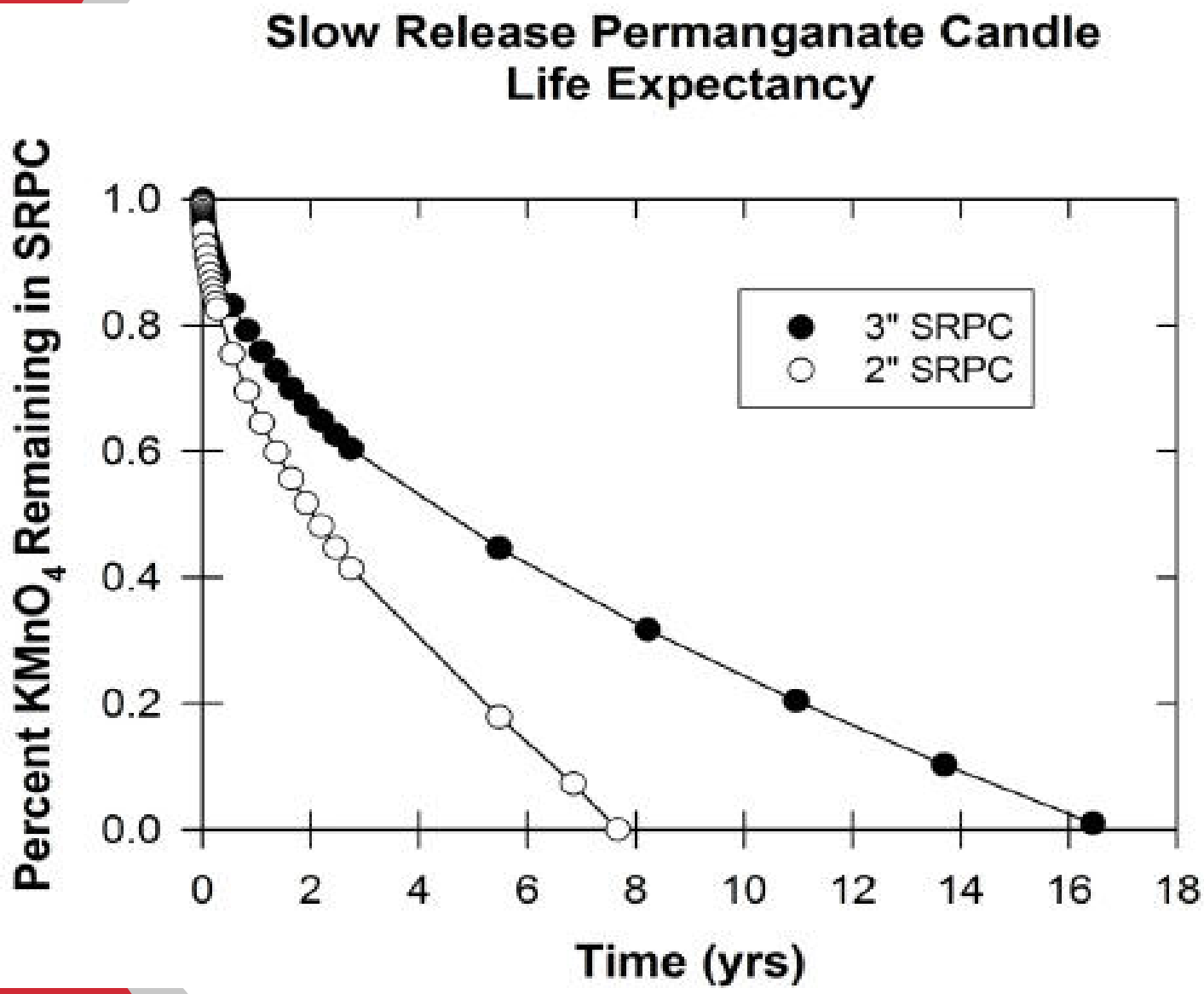
Results

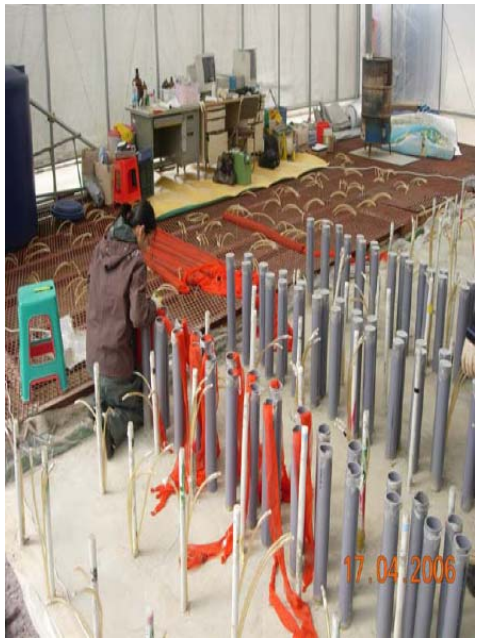
8 year life expectancy for 2” SRPC

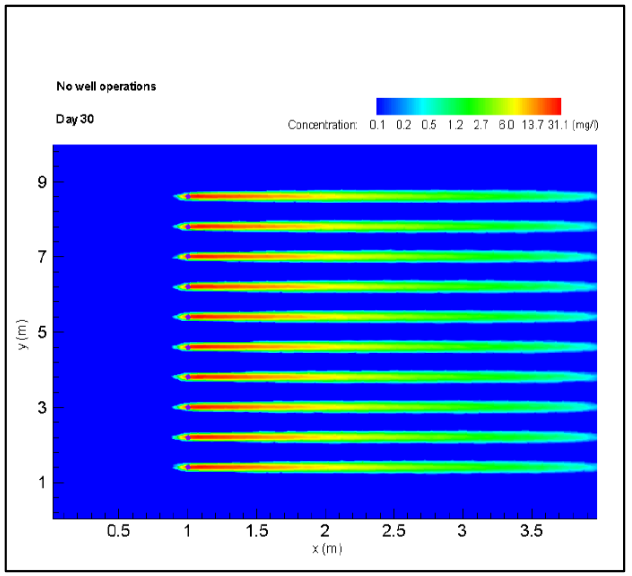
16 year life expectancy for 3” SRPC



Next Steps...Exploring Key Issues

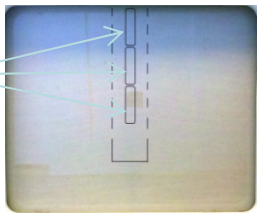
- Slow-release permanganate candles installed in wells (Lee and Schwartz, 2007)
- Lack of lateral dispersion could reduce treatment efficiency
- Requires close spacing of candles
- With wide spacing need ways to provide mixing...



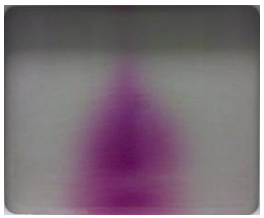


Mini-candles in saturated tanks with and without re-circulator

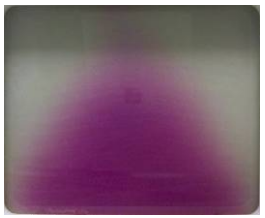
Candle Location



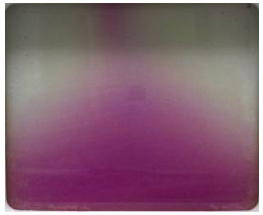
T = 0



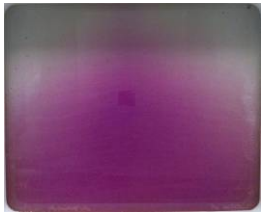
1 day



2 days



3 days

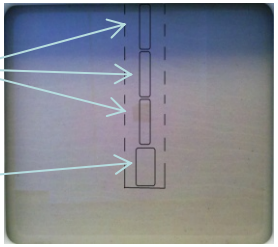


4 days

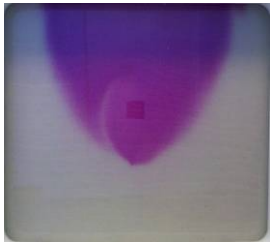
5 days

Candle Location

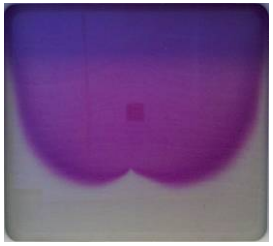
Re-circulator



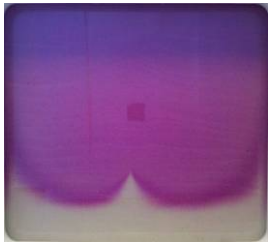
T = 0



15 min



30 min



45 min

60 min

75 min

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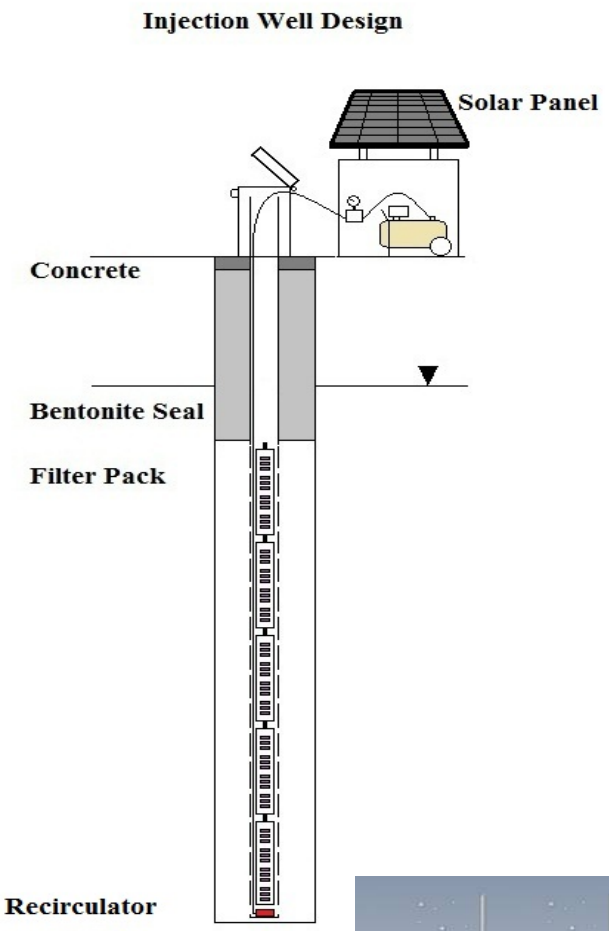
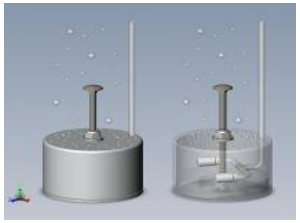
Proposed Modification to Current Treatment



Candles with solar-powered recirculator



After inserting the recirculators (and 342 days after candles were installed) there is a 64%-100% reduction in TCE

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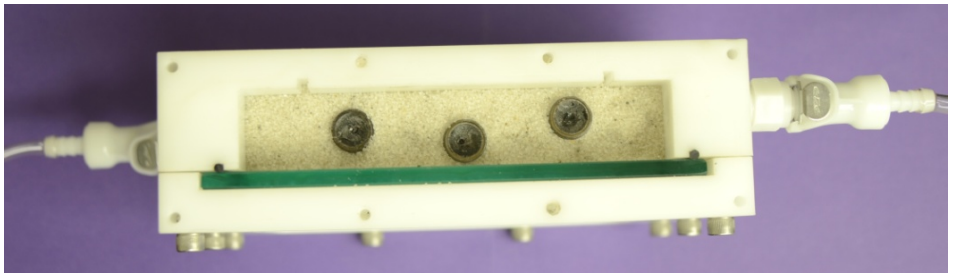
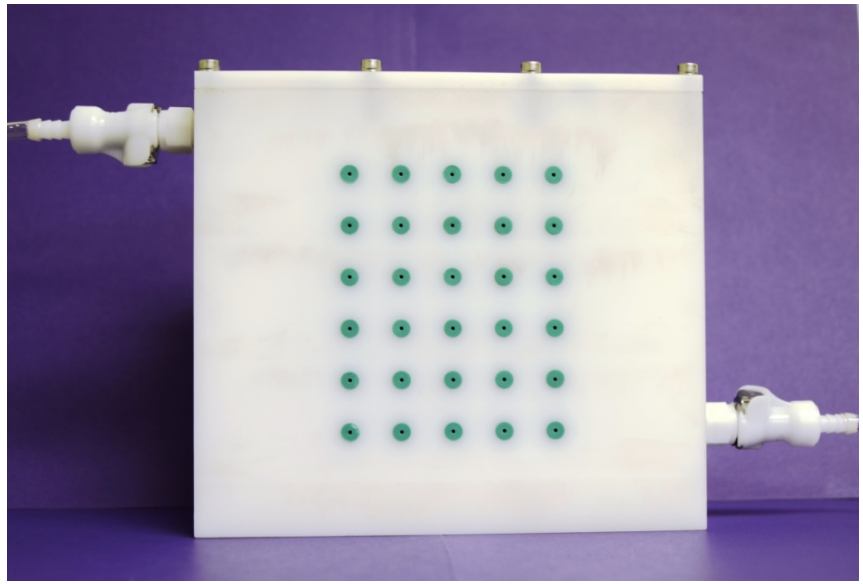
Next Steps – Column and Tank Experiments (80% $KMnO_4$) & Mfg



1 cm diameter x 9 cm length

3.8 cm diameter x 5.1 m length



Conclusions

- Direct push or in-well applications for source or barrier treatment that may last years
  - Potential for application in low permeability soils, fractured bedrock
  - Dry cleaners: passive *in situ* treatment without above ground equipment/infrastructure
- Cost savings realized with direct push delivery
- Money spent on the treatment vs. man power, injection well installation

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