

Coupling Surfactants with Permanganate for DNAPL Removal: Coinjection or Sequential Application as Delivery Methods

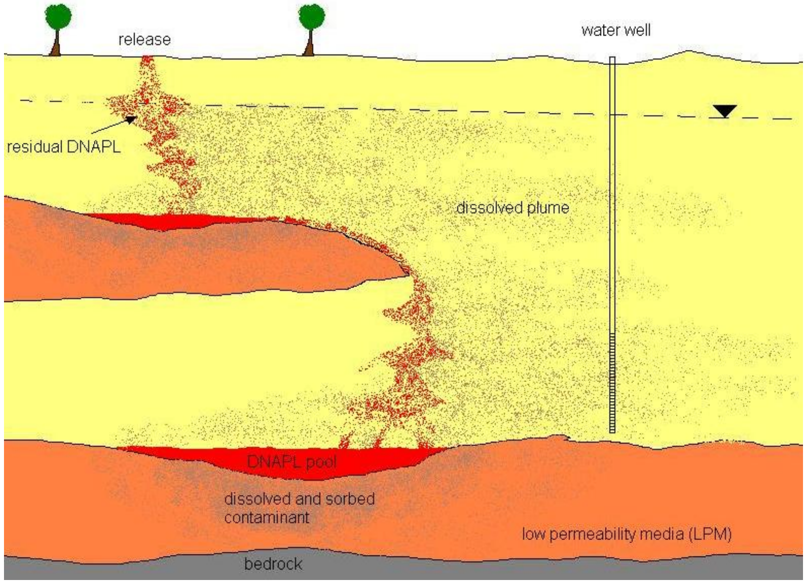
Pamela J. Dugan, Ph.D., Carus Corporation
Robert L. Siegrist, Ph.D.
Colorado School of Mines
Michelle L. Crimi, Ph.D., Clarkson University

Today’s Agenda

- Motivation for surfactant-enhanced permanganate
- Background:
  - Surfactants/permanganate
- Experimental approach, results, concluding remarks
- Recent work and next steps
- Questions

The Problem...Dense Nonaqueous Phase Liquid (DNAPL)

- Wide-spread global environmental problem due to low aqueous solubility and denser than water, able to migrate to great depths in an aquifer



Source: Heiderscheidt, 2005

•Once DNAPL enters the environment it can pollute *many millions of gallons of groundwater* with huge dissolved plumes that serve as *long-term sources of contamination* (e.g., *many decades*)

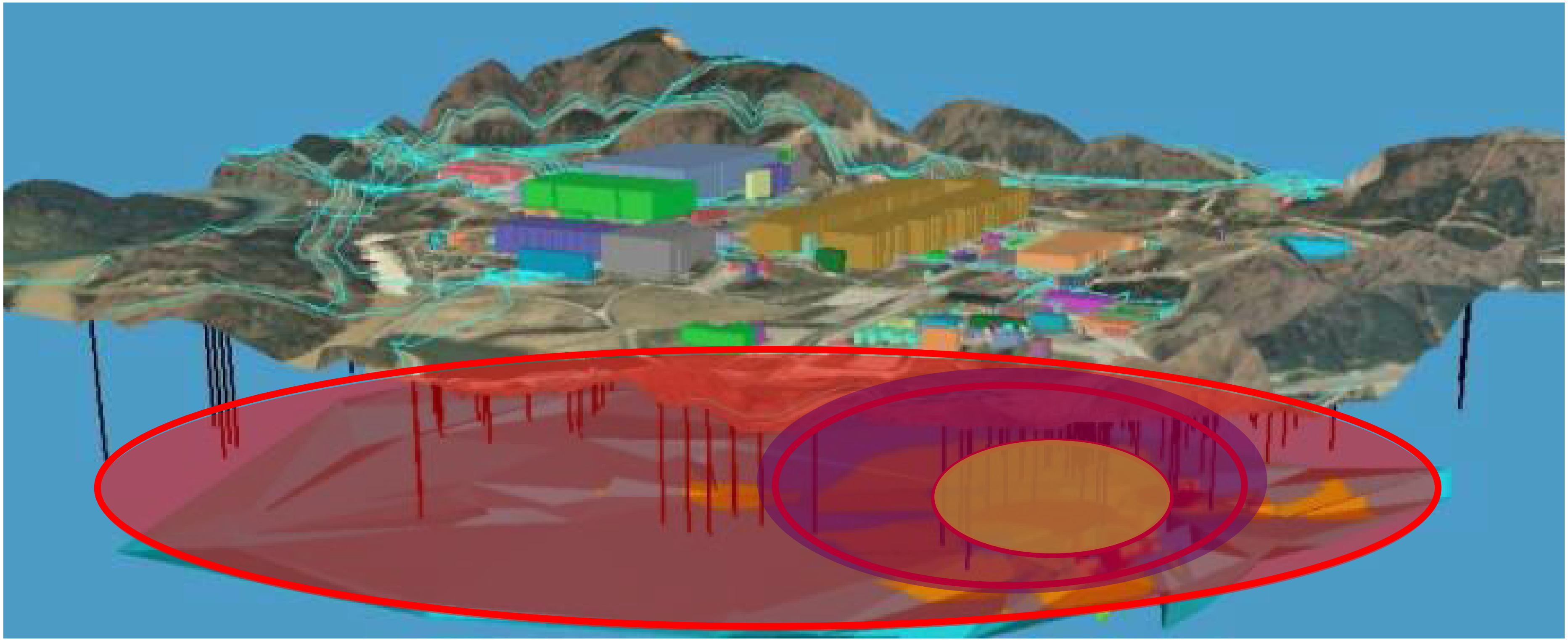
The Problem...DNAPL

- Examples are trichloroethene (TCE) & percholorethene (PCE)
  - Used to clean metal parts of machinery and in dry cleaning applications
  - These compounds are *<u>toxic and carcinogenic</u>* and very difficult to remediate

Motivation- Surfactant-Enhanced Permanganate

- Inadequacy of pump-and-treat for DNAPL mass removal has been well documented (e.g., Kavanaugh 2003, NRC 2005)
- Optimized remedial strategies often require multiple technologies to reach performance goals (i.e., treatment train)
  - For example, coupling surfactant-enhanced aquifer remediation (SEAR) with *in situ* chemical oxidation (ISCO)
- Treatment train can occur sequentially, concurrently, or spatially within a contaminated site

Coupling Remediation Technologies

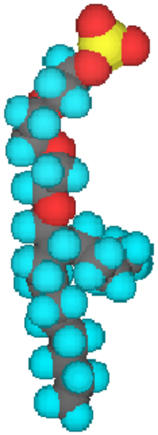


Dissolved Plume
Bio, MNA ,
ISCO (for speed)

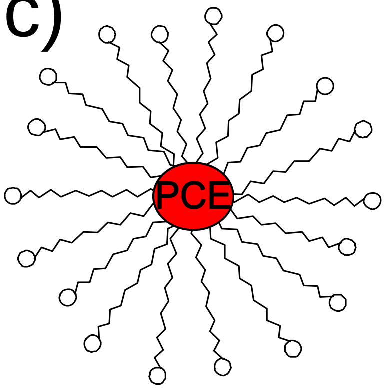
Core Plume
ISCO, Bio,
P-and-T

Source Zone
SEAR, ISCO,
Excavation,
Thermal

Surfactant-Enhanced Aquifer Remediation (SEAR)

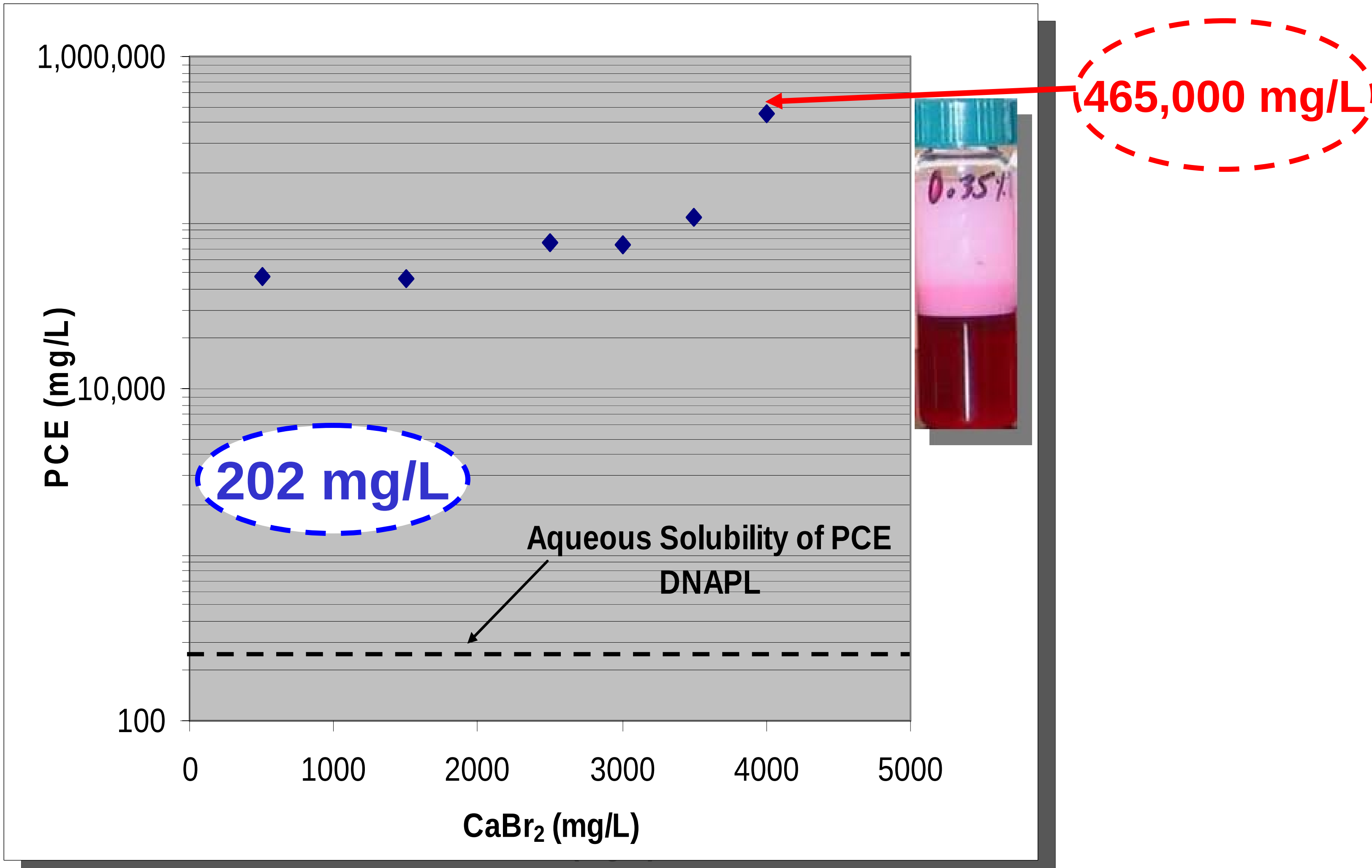


- Surfactants-Surface-Active Agents
  - Hydrophilic head/hydrophobic tail
  - Above the critical micelle concentration (CMC) form structures that alter properties of organic-water interface (anionic, nonionic)
  - Can enhance DNAPL removal by solubilization/mobilization



- Surfactants are very useful for treating DNAPL *not* dissolved phase contaminants

Surfactant-enhanced DNAPL solubilization



In Situ Chemical Oxidation (ISCO)

- Delivery of oxidants into the subsurface to destroy organic contaminants in soil and ground water

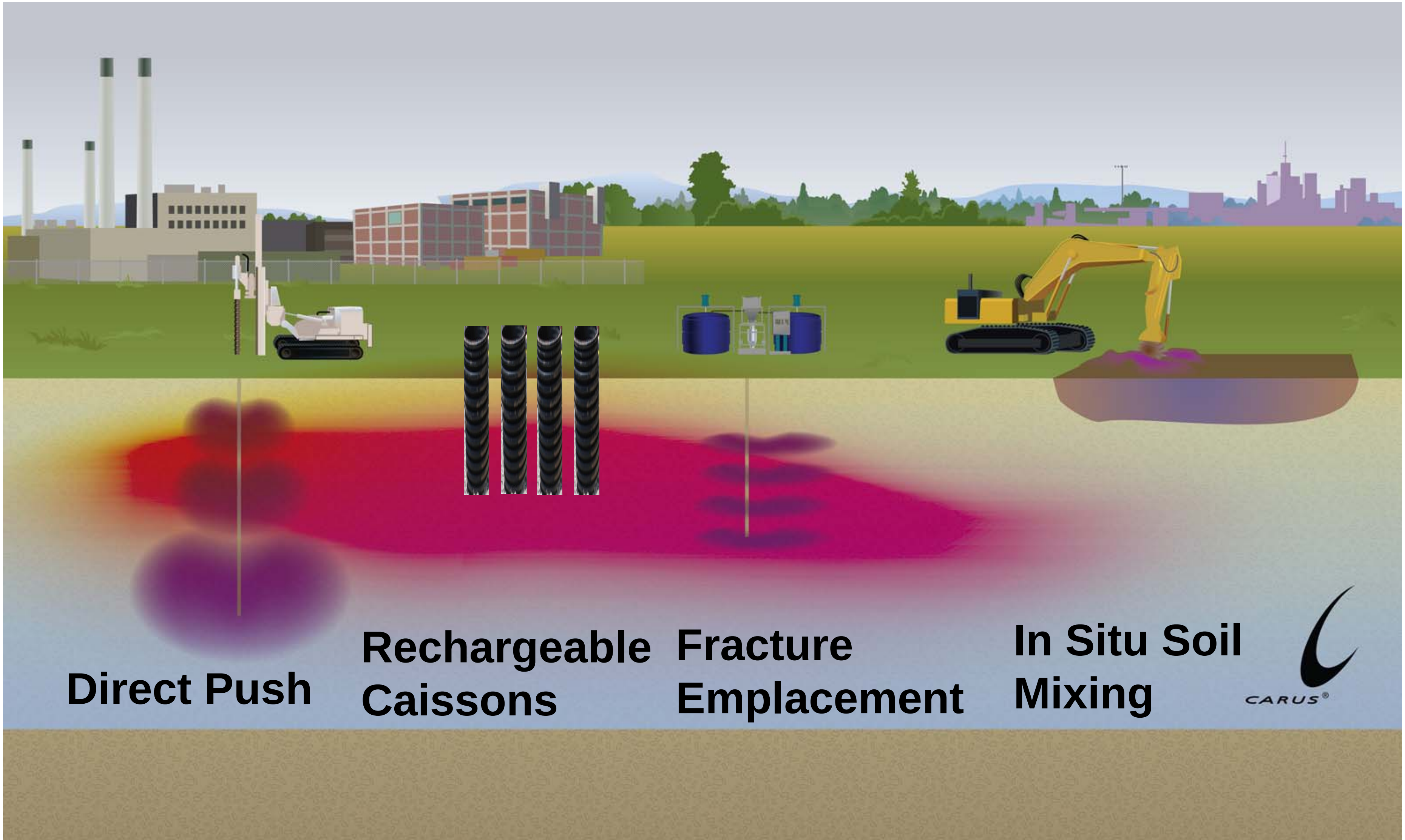
RemOx® S ($KMnO_4$) and RemOx® L ($NaMnO_4$)

PCE:

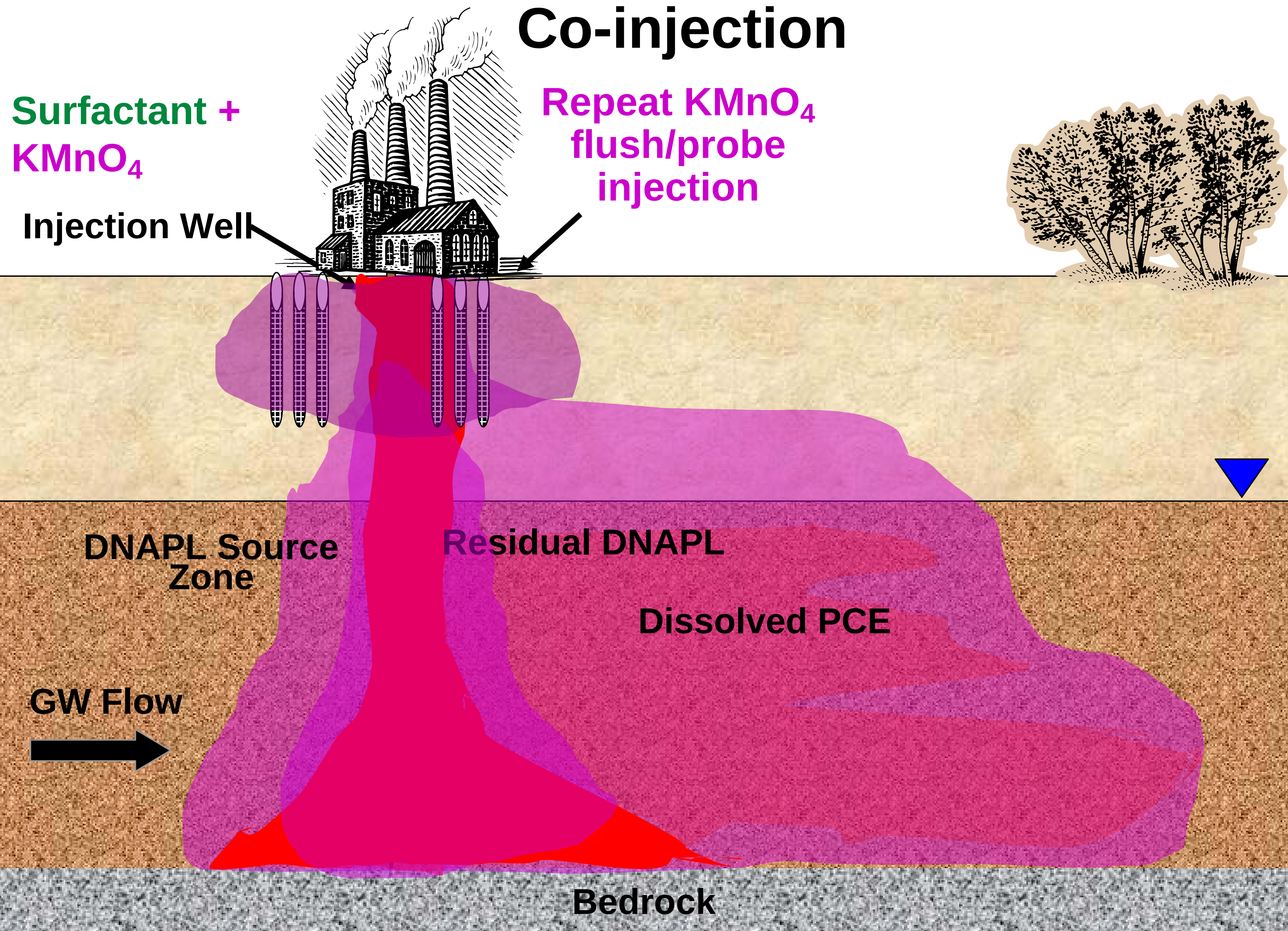
$3C_2Cl_4 + 4KMnO_4 + 4H_2O \rightarrow 6CO_2 + 4MnO_{2(s)} + 4K^+ + 8H^+ + 12Cl^-$

- Permanganate is very good at treating dissolved phase contaminants...not very useful treating large masses of DNAPL

ISCO Delivery Technologies

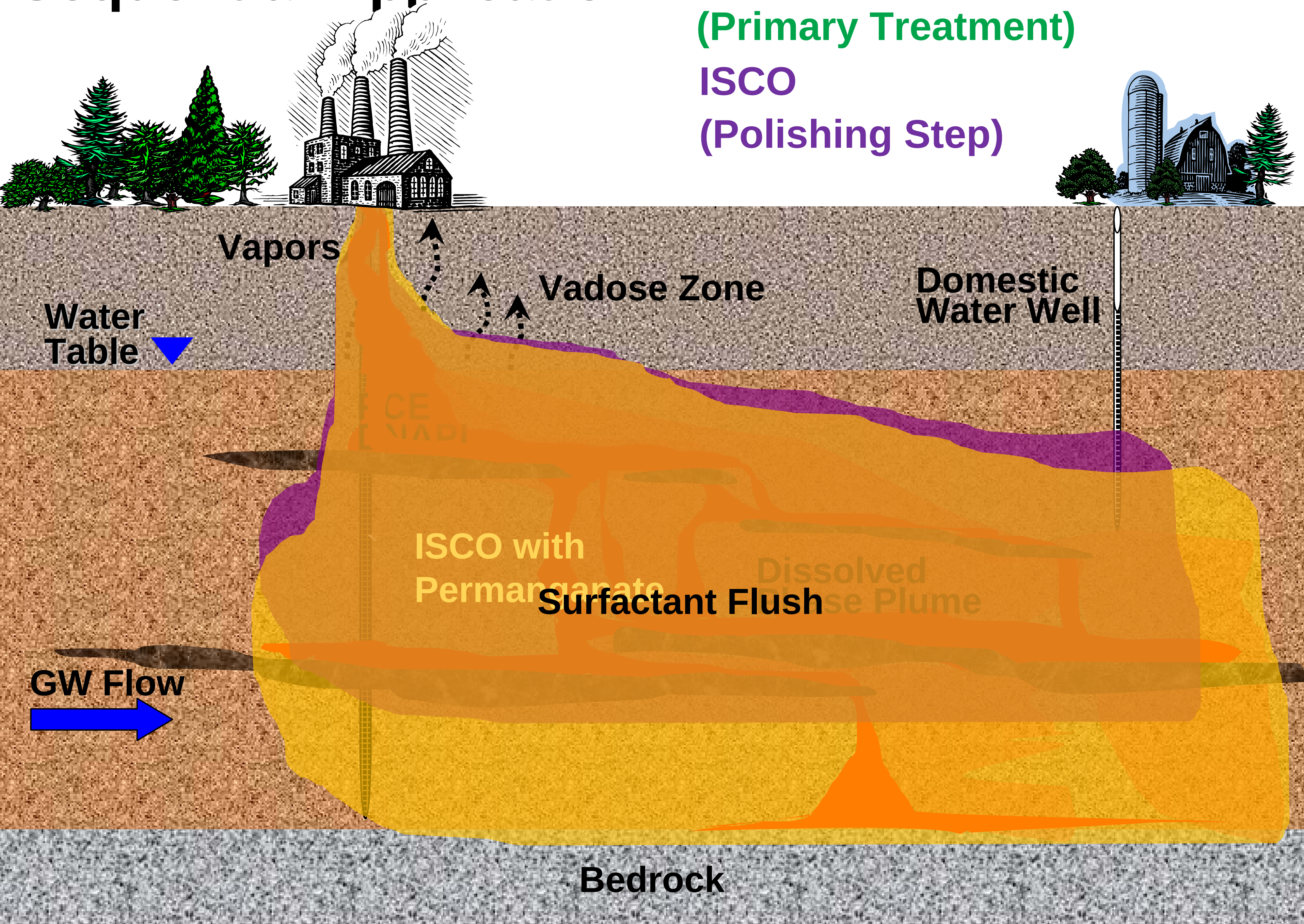


Co-injection



Sequential Application

SEAR
(Primary Treatment)
ISCO
(Polishing Step)



Coupling SEAR with ISCO – Economic Implications

- Surfactant costs can be significant…
  - At higher concentrations (e.g., 4-8 wt%) could likely be the largest individual project cost
  - Using more pore volumes (PVs) also increases project costs significantly
- When properly designed…
  - Cost savings could be realized by using lower concentrations of amendments (e.g., < 2 wt%) as well as fewer PVs of flushing



Coupling SEAR with ISCO – Remediation Implications

- ISCO is typically not well-suited for removal of high saturation/pooled DNAPL zones
- SEAR not useful for plume treatment-can only be used for DNAPL mass removal
- Potential sequential application advantages…
  - SEAR for removal of large masses of DNAPL
  - ISCO as a polishing step
- Potential coinjection advantages…
  - Potential for “inject and leave”...less time spent in field
  - No aboveground treatment of fluids

Experimental Approach

- Batch experiments:
  - Coupling surfactants/cosolvents with $KMnO_4$
  - Goal: find compatible pairings for use in 2-D cell studies
- 2-D flow-through cell experiments:
  - Evaluate two SEAR/ISCO delivery methods
  - Remedial goal: **> 90% mass removal** using **low surfactant/oxidant conc.'s** with **< 1 PV** flushing

Delivery Methods

- Co-injection:
  - Coupling surfactant-enhanced solubilization of DNAPL with ISCO for DNAPL mass destruction in a ***single step***
- Sequential application:
  - Coupling surfactant-enhanced solubilization of DNAPL ***followed by*** polishing with ISCO

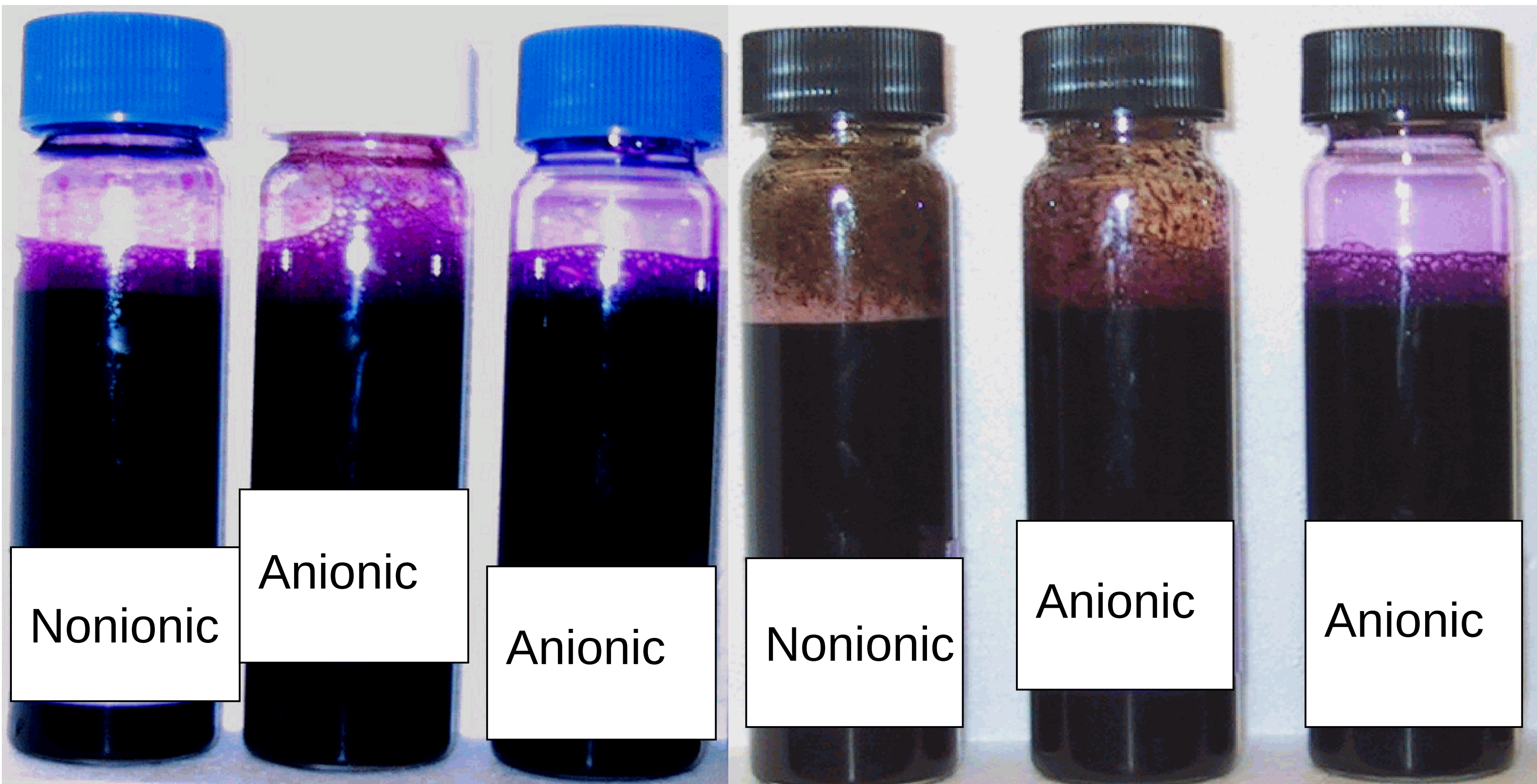
Approach – Batch Experiments

- Batch screening tests with 72 surfactants (anionic and nonionic) with $KMnO_4$

- Compatibility Criteria:
  - Relatively low oxidant demand (< 25% of oxidant consumed after 24-hour reaction period)

Results – Batch Experiments

0.01-wt% **1.0-wt%**



Approach
2-D Flow-Through Cell Studies

Cell dimensions: 30 cm. x 30 cm. x 4 cm.

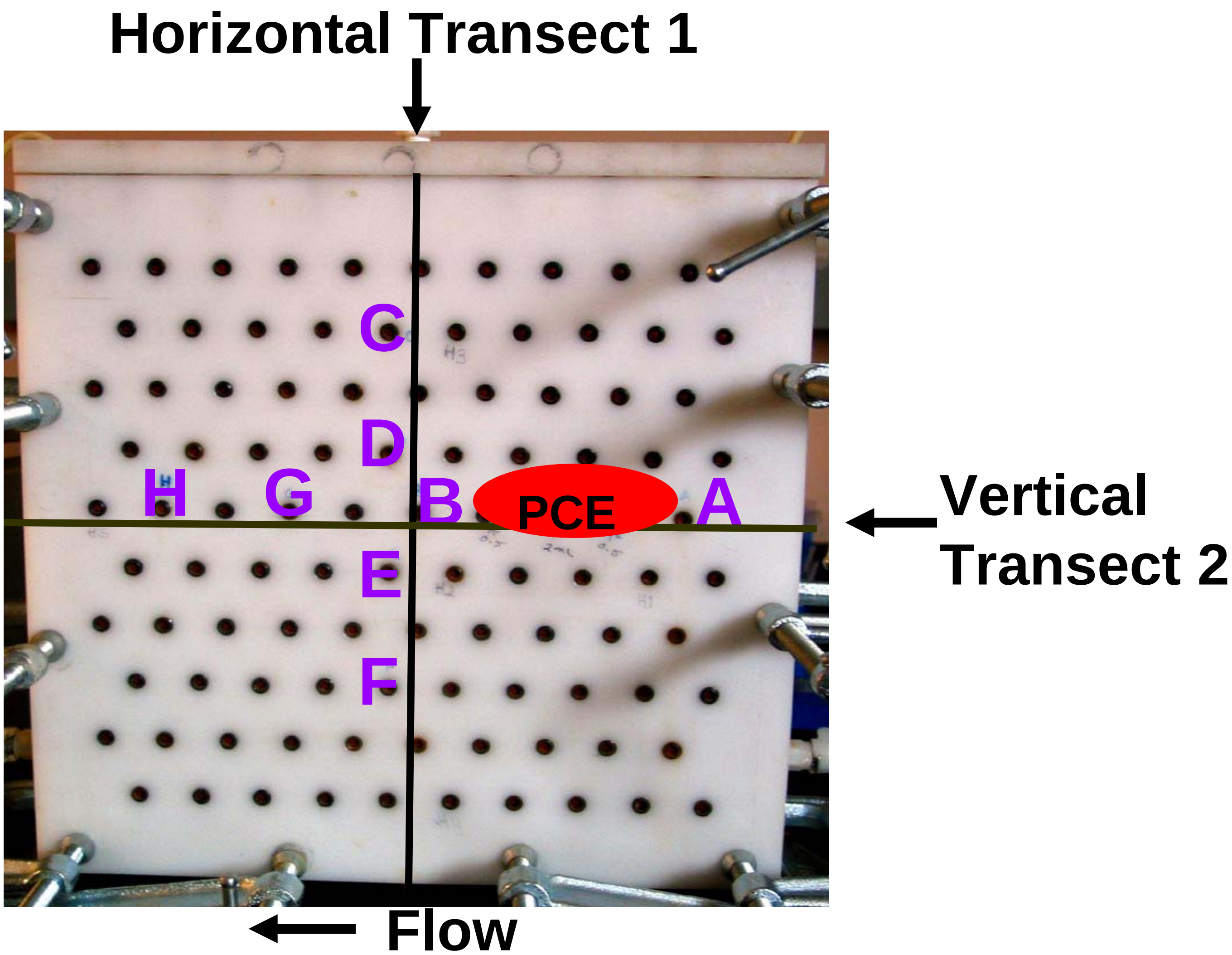
Fine-grained matrix K_{sat}=0.02 cm/sec

Coarse lens K_{sat}=0.3 cm/sec

PCE DNAPL pool ~ S_N 11%

Influent port **Flow** **Effluent port**

Approach
2-D Flow-Through Cell Studies



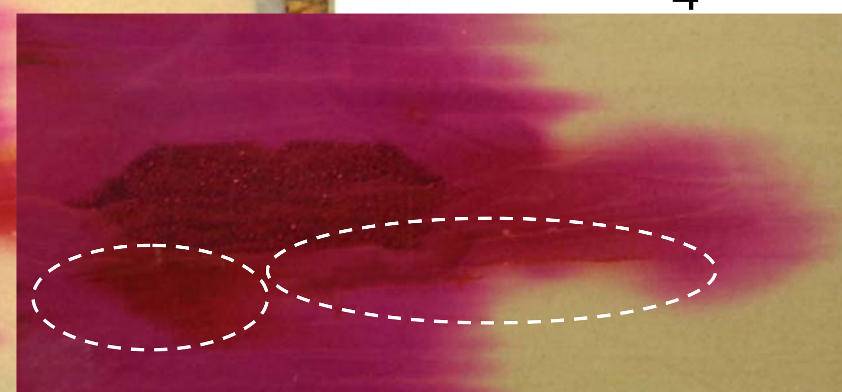
Methods – Co-injection

- Co-injection solution/methods: US Patent 7553105
  - 1.5-wt% surfactant/co-surfactant, 0.35-wt% $CaBr_2$, 0.75-wt% NaBr (1.5-wt%$_{total}$)
    - PCE solubility: 202 → 465,000 mg/L
    - DNAPL solubilization/mobilization as removal mechanisms
  - 0.5-wt% $KMnO_4$

Methods – Co-injection

- PCE added: 3.82 g
- Cell PV = 1.5L
- Natural dissolution: 0.9 mL/min (12 cm/day)
- 0.66 PVs of surfactants with permanganate were injected in a *single step*
- Flushing flow: 3.8 mL/ min (52 cm/day)
- PCE, chloride, and $KMnO_4$ samples (8 point sampling ports and effluent)
- 2-D cell extracted in hexane at conclusion

Co-injection



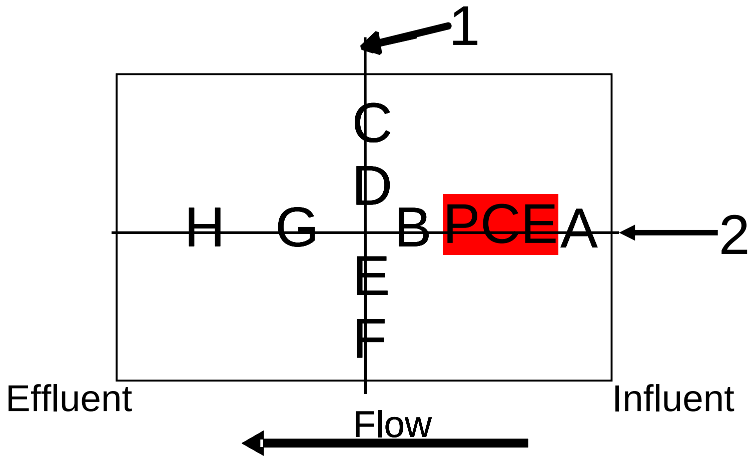
0.66 PVs of 1.5-wt% surfactants *with* 0.5-wt% $KMnO_4$

Results – Co-injection

Transect 1

	Pre-flush	During flush (0.2 PV)	3-days post
C	0	0	0
D	0	0	0
E	34	8238	0
F	0	0	47

Conclusion (2 weeks-post) all ports =0



Effluent

Pre-	18
During (0.2 PV)	30
3-days post	14
Conclusion	0.002

Transect 2

	H	G	B	A
Pre-flush	35	80	65	0
During (0.2 PV)	68	109	2052	110
3-days post	0	0	0	0

Conclusion (2 weeks-post) all ports = 0

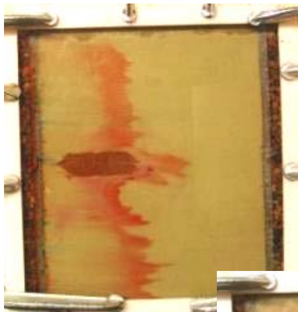
Units = mg-PCE / L

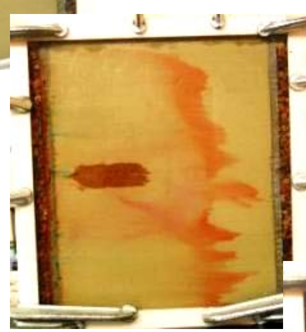
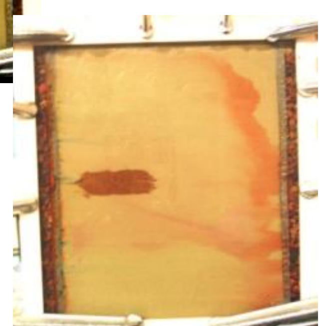
Methods – Sequential

- Sequential flushing solution:
  - 0.66 PVs of surfactants and electrolytes (1.5-wt%) *followed by:*
  - 0.66 PVs of 0.5-wt% $KMnO_4$ in SGW
  - PCE added: 3.68g
  - Natural dissolution: 0.9 mL/min (12 cm/day)
  - Flushing flow: 3.8 mL/min (52 cm/day)
  - Samples: PCE (SEAR), PCE, Cl^-, $KMnO_4$ (ISCO)

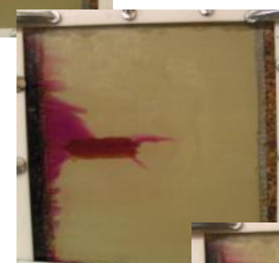
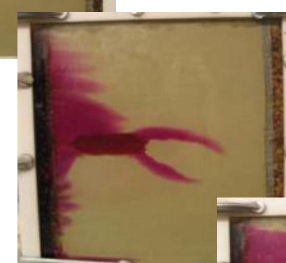
Results – Sequential

1. 0.66 PVs of 1.5 wt% surfactants



2. *Followed by* 0.66 PVs of 0.5 wt% $KMnO_4$

Results – Sequential

Treatment Steps	Natural Dissolution DNAPL Removed (%) (PCE effluent)	Step 1: SEAR DNAPL Removed (%) (PCE effluent)	Step 2: ISCO DNAPL Removed (%) (Cl^- effluent)
Step 1: 0.66 PV of 1.5-wt% surfactants, electrolytes Step 2: 0.66 PV of 0.5 wt% $KMnO_4$	11.2	84.2	4.6

Performance Assessment

Delivery Method	Total PCE DNAPL Removed (extraction)
Co-injection- Surfactants with $KMnO_4$ ***in a single step***	**99.8%**
Sequential Application- Surfactants ***followed by*** **$KMnO_4$**	**100%**

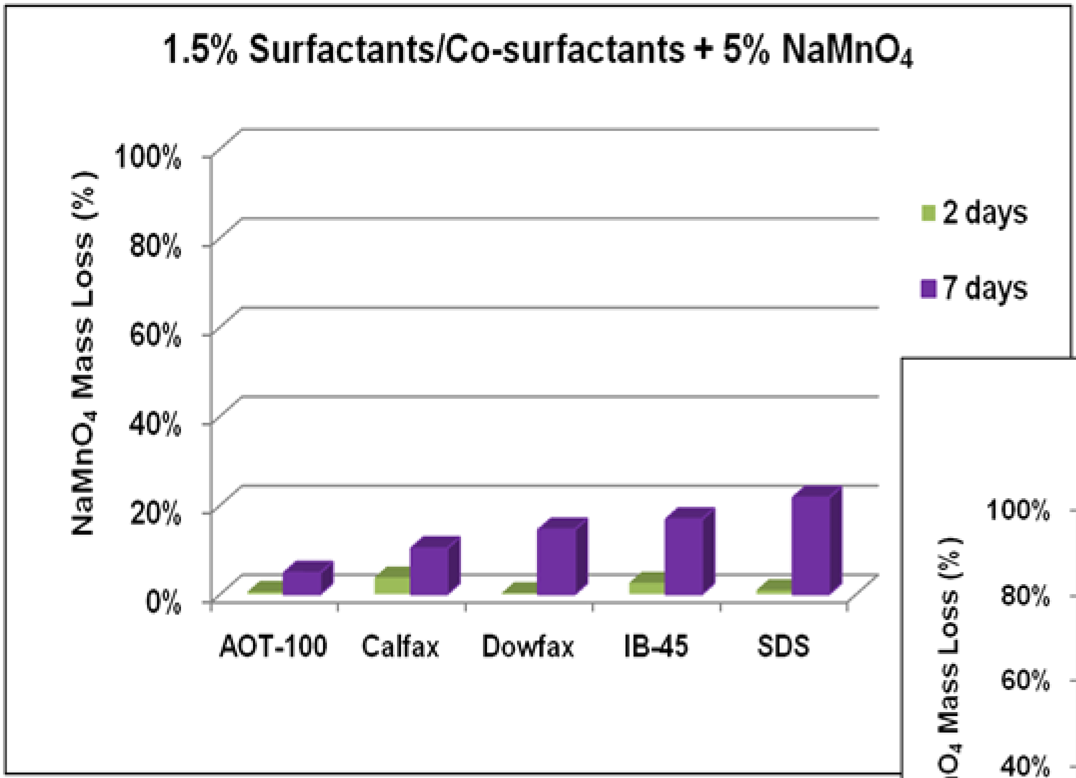
- Reached remedial goal - low conc's < 1 PV of flushing >90% removal PCE DNAPL

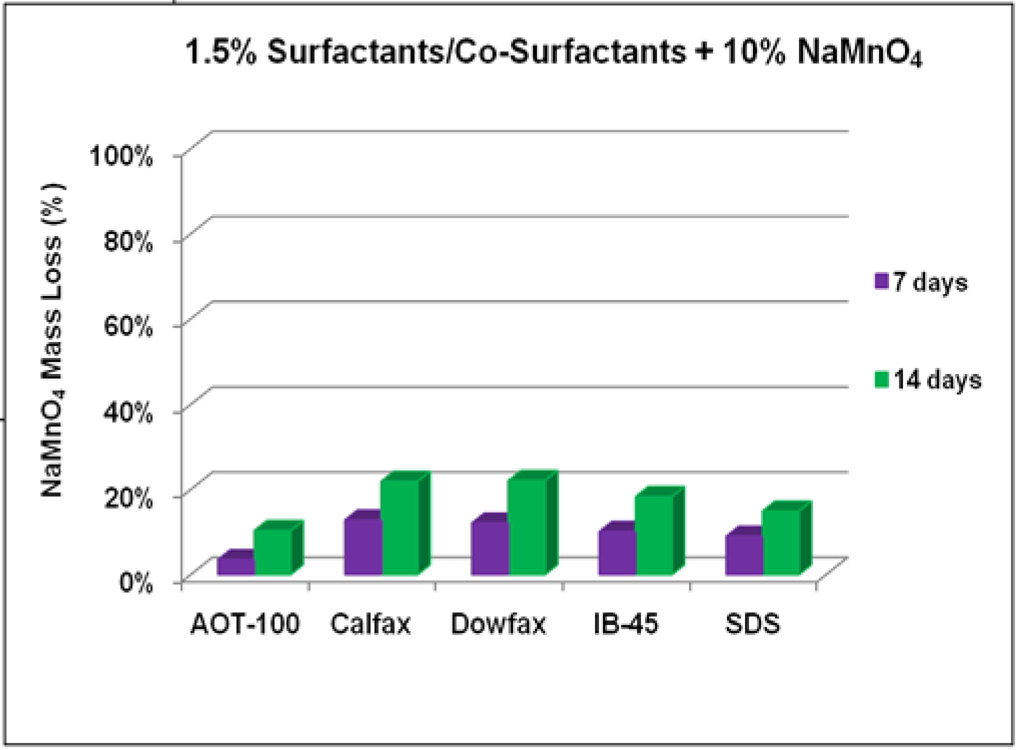
CARUS®

Conclusions

- Batch experiments:
  - 4 surfactants were found to be compatible with permanganate (< 25% mass loss in 24-hr reaction period)
- 2-D cell studies:
  - Reached remedial goal of >> 90% DNAPL removal using relatively low surfactant/oxidant concentrations and < 1PV of flushing

Recent Developments – Effect of Permanganate Concentration





Current and Future Work

- Dugan, Crimi, and Siegrist. (2010). “Coupling surfactants/cosolvents with oxidants for enhanced DNAPL removal: A review.” Remediation Journal, 20(3), 27-49.

- Kinetic studies for optimization of surfactant-enhanced permanganate oxidation of DNAPL

- Collaboration with Dr Michelle Crimi (Clarkson University)
  - Surfactant- and polyphosphate-enhanced permanganate oxidation of DNAPL through MnO_2 particle stabilization: 2-D flow through cell experiments

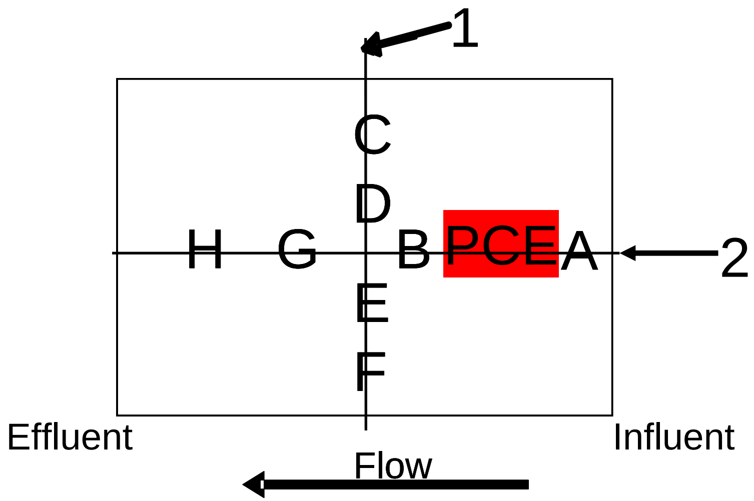
Thank you!
Questions?

pamela.dugan@caruscorporation.com

Results – Sequential (SEAR)

Transect 1

	Pre-SEAR	During (0.4PV)	3-days post
C	0	0	0
D	0	0	0
E	28	36481	0
F	0	0	24



Transect 2

	H	G	B	A
Pre-SEAR	40	68	69	0
During (0.4 PV)	18	59	3225	0
3-days post	0	0	0	0

Effluent

Pre-SEAR	27
During	24
3-days post	165

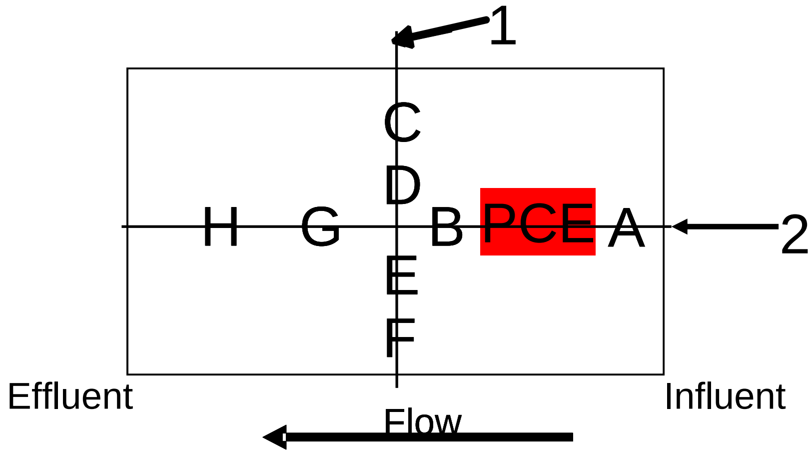
Units = mg-PCE / L

Results – Sequential (ISCO)

Transect 1

	Pre-ISCO	During (0.4PV)	3-days post
C	0	0	0
D	0	0	0
E	91	0	0
F	0	0	0

Conclusion (24 days post-ISCO) all ports = 0



Transect 2

	H	G	B	A
Pre-ISCO	0	0	0	0
During (0.4PV)	0	34	64	0
3-days post	0	0	0	0

Conclusion (24 days post-ISCO) all ports = 0

Effluent

Pre-ISCO	165
During (0.4 PV)	83
3-days post	26
Conclusion	BDL

Units = mg-PCE / L