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FIELD TEST OF ELECTROKINETICALLY-ENHANCED THERMALLY ACTIVATED PERSULFATE FOR REMEDIATION OF CHLORINATED SOLVENTS IN CLAY

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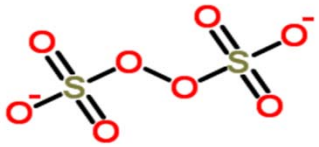
Introduction

Persulfate (ISCO)



Persulfate ($S_2O_8^{2-}$): a strong oxidizing agent used for in-situ chemical oxidation (ISCO) of organic contaminants

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad \boldsymbol{E^0 = 2.01\ V}$$

Common Oxidants	Standard Reduction Potential, V
Persulfate	+2.6
Permanganate	+1.7
Hydrogen Peroxide	+1.77
Ozone	+2.1

With heat activation (i.e., thermolysis):

$$S_2O_8^{2-} \xrightarrow{Heat.} 2SO_4^{\bullet -} \qquad \boldsymbol{E^0 = 2.6\ V}$$

*Activation results in an increase in reduction potential and reaction kinetics along with a decrease in selectivity towards contaminants

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Introduction

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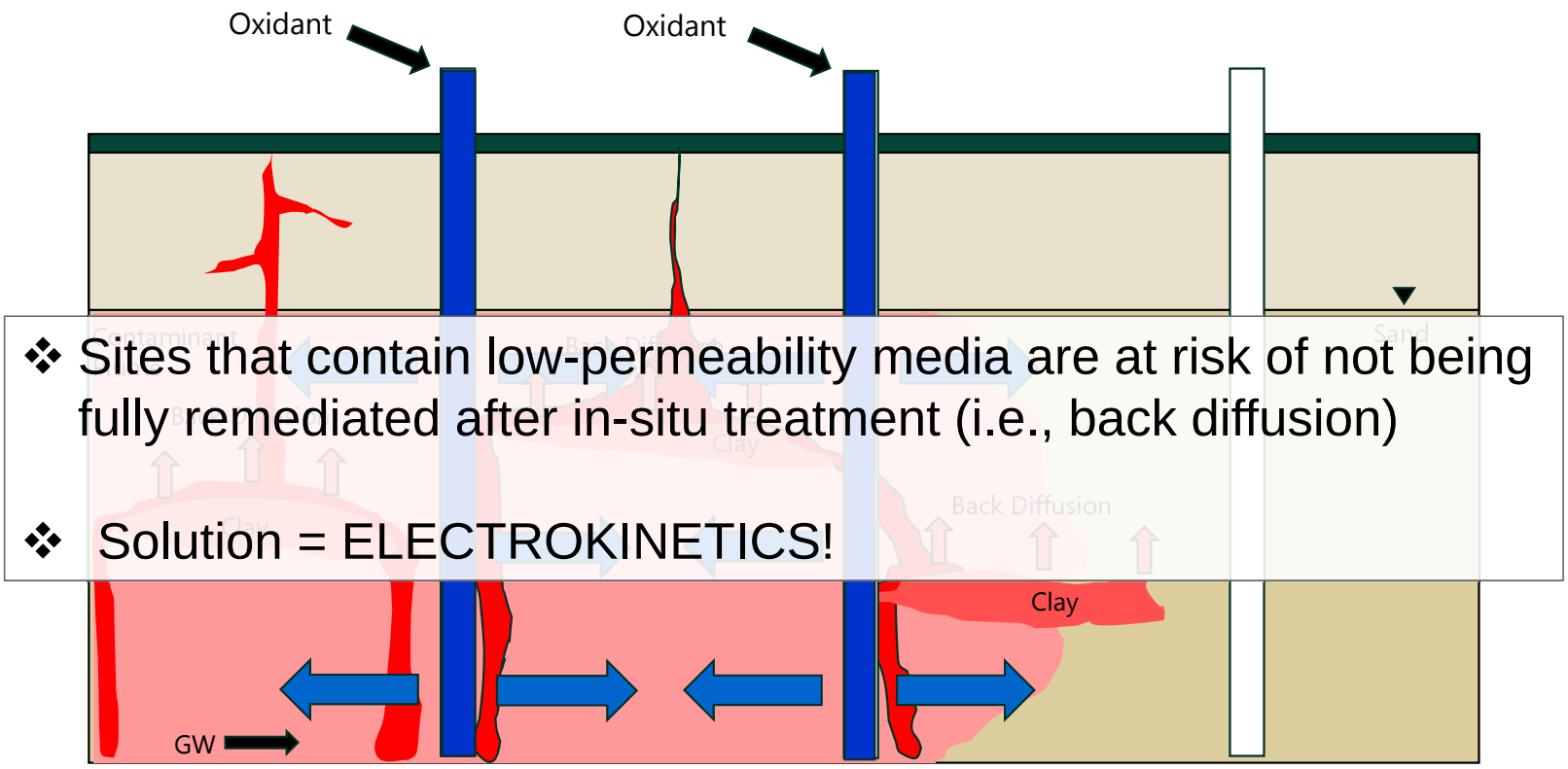

- Sites that contain low-permeability media are at risk of not being fully remediated after in-situ treatment (i.e., back diffusion)
- Solution = ELECTROKINETICS!

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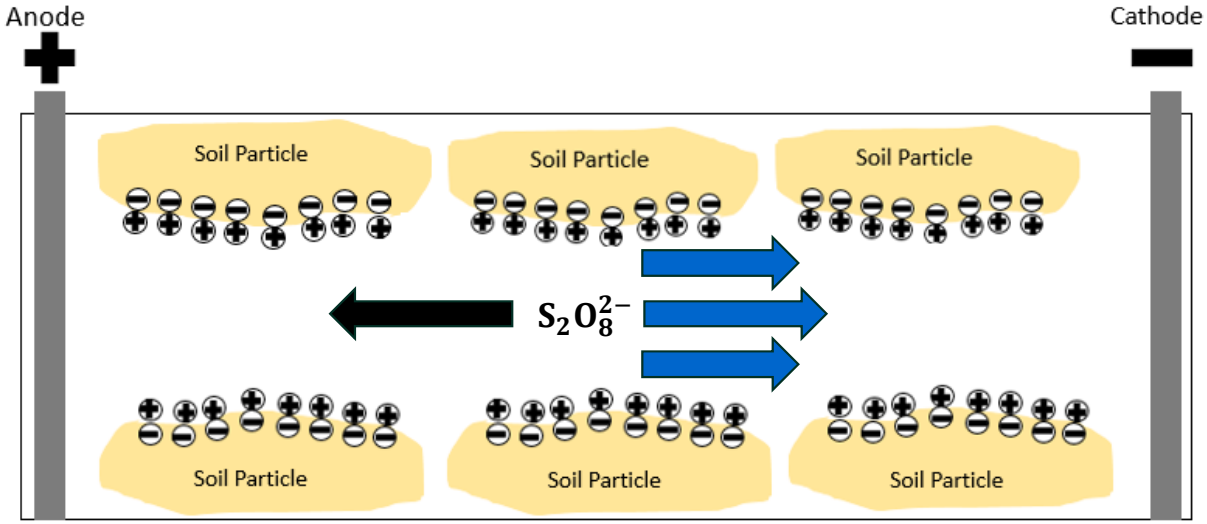
Introduction

Electrokinetics (EK)

- **EK** is application of a low-voltage direct-current across a section of soil to enhance the movement of charged particles (e.g., ions) and water. Primary mechanisms:

1. **Electroosmosis (EO):** movement of bulk fluid towards cathode

2. **Electromigration (EM):** movement of charged ions and species towards oppositely charged electrode



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Electrokinetics (EK)

	6 hrs	12 hrs
Hydraulic Injection		
Hydraulic Injection + EK		

Chowdhury et al., *Water Research,* 2017

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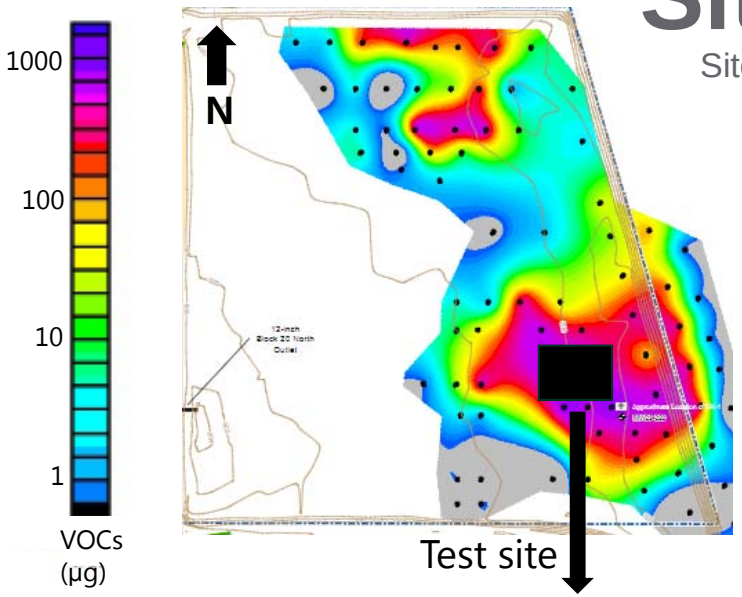
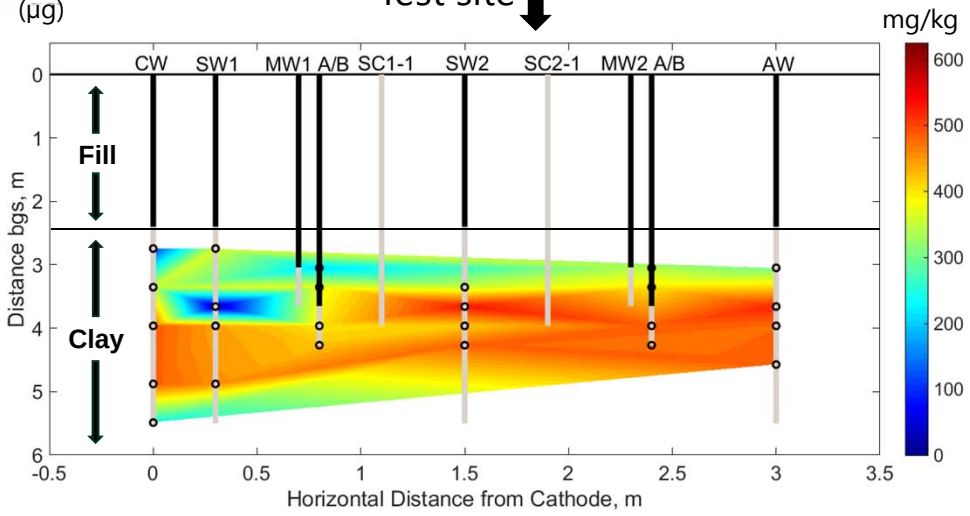
EK-Enhanced Thermally Activated Persulfate (EK-TAP)

- **EK-TAP:** Electrokinetically-enhanced thermally activated persulfate
  - Persulfate is delivered by EK (direct-current) and thermally activated by low-temperature electrical resistance heating (ERH) (alternate-current)
- Shown success at the bench-scale (Chowdhury et al., *ES&T,* 2017)
- **How will EK-TAP perform at the field-scale?**

Site Description

Site History, Geology, and Contamination





- Site located in SW Ontario, Canada
- Former drum storage area for vinyl chloride production (1942-2006)
- 2.4 m of fill underlain by 15 m of clay
- Target Contaminants:
  - 1,2-DCA
  - 1,1-DCA
  - 1,1,2-TCA
  - VC
  - TCE

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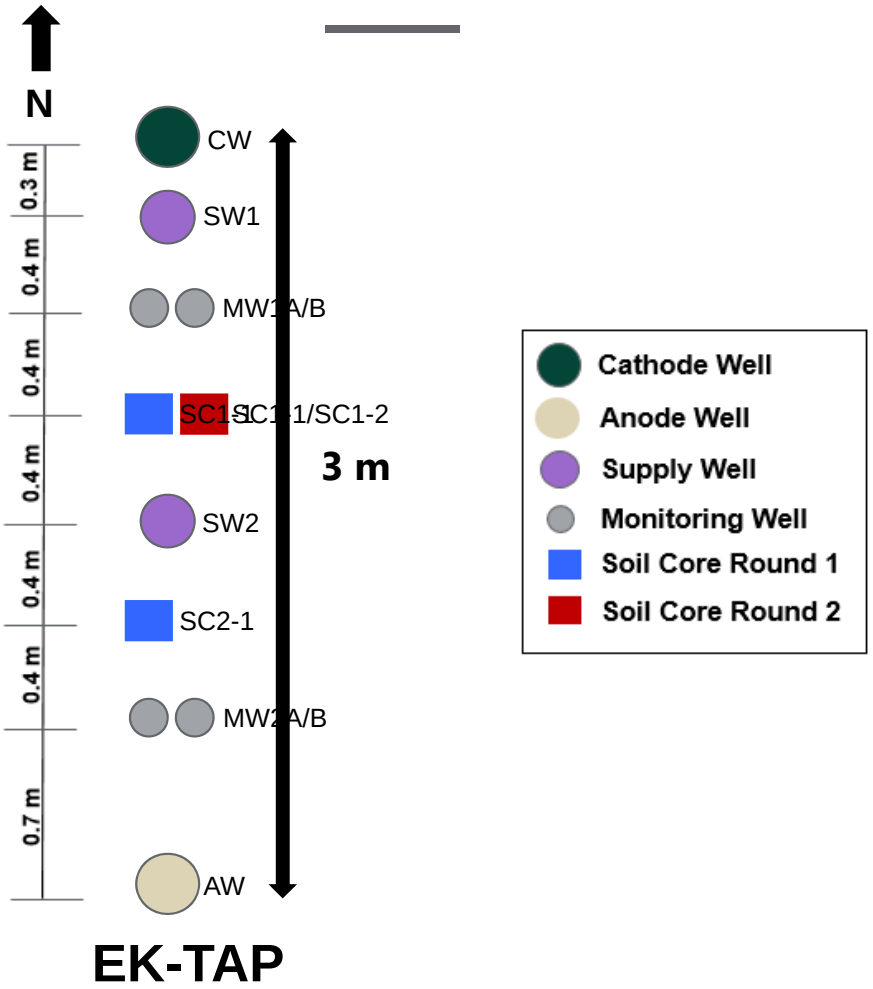
Site Implementation

Plan View of Site



EK-TAP

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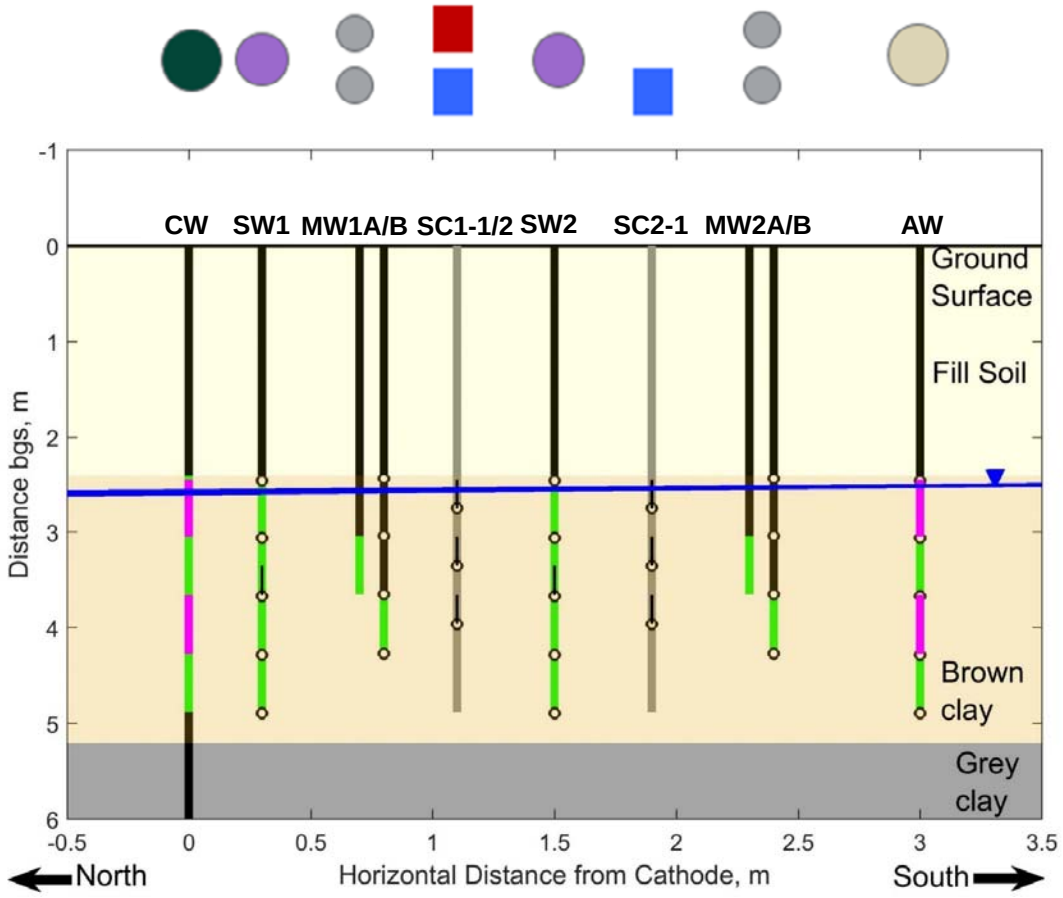
Plan View and Cross-Section of Site



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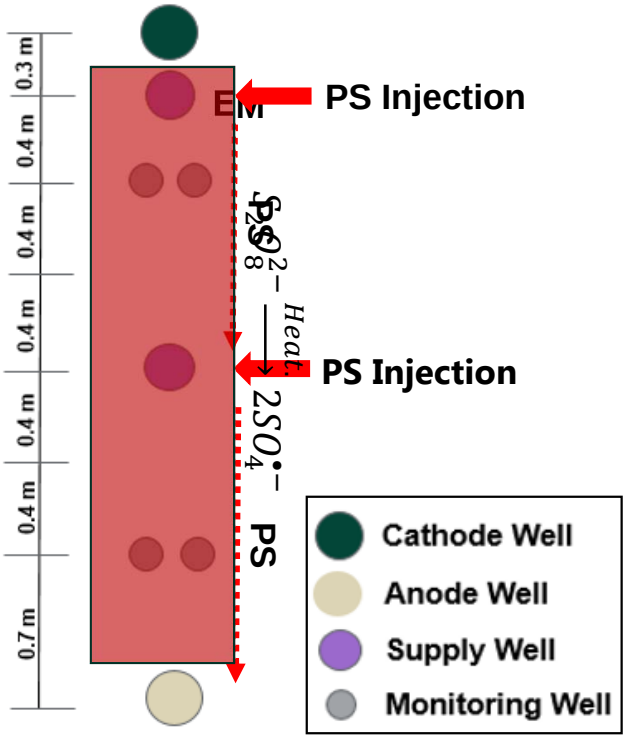
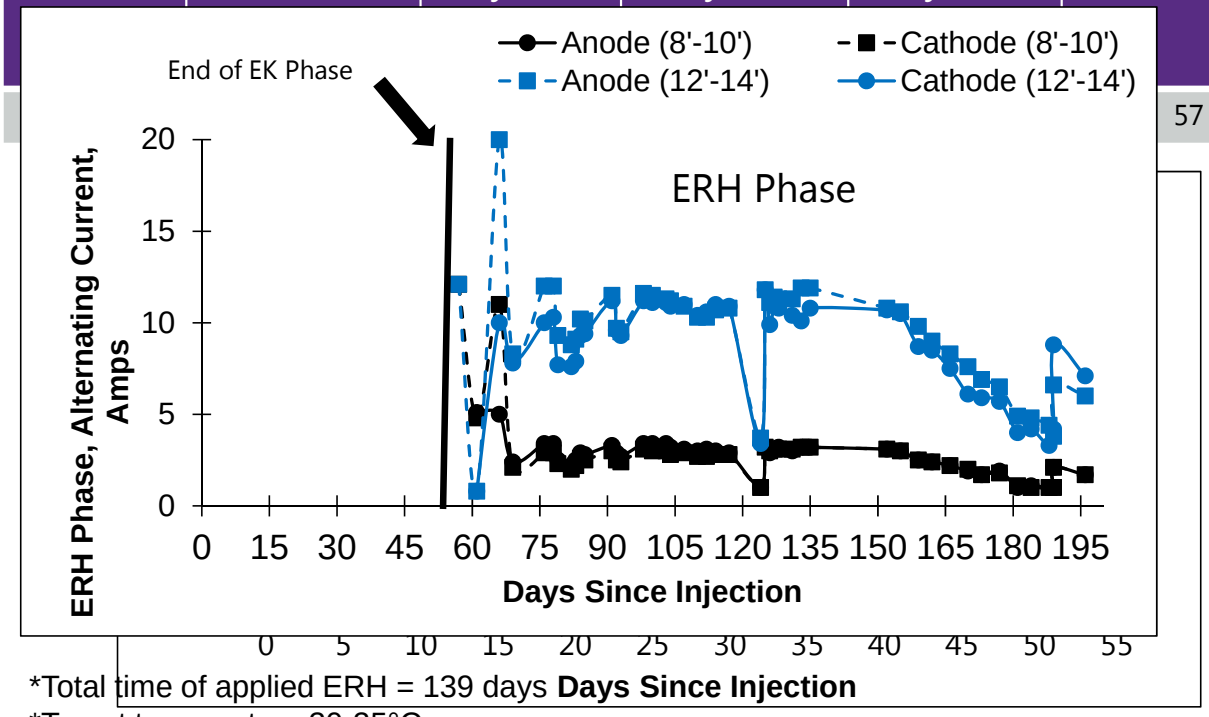
Site Implementation

Persulfate Injection, EK-Enhancement, and ERH Thermal Activation



Transect	Amendment	Injected	Injected	Injected	Duration, [days]
					57



*Total time of applied ERH = 139 days **Days Since Injection**

*Target temperature 30-35°C

*Total time of applied current = 40 days

*Total time target amperage (9A) achieved = 22 days

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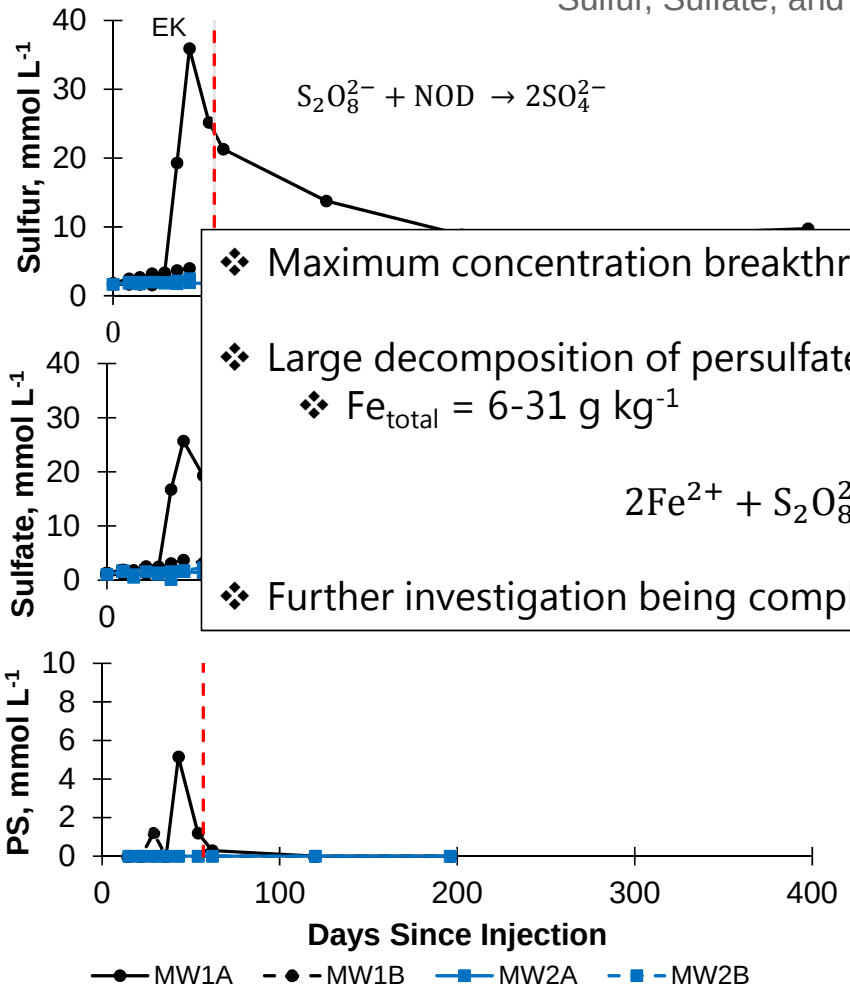
Study Objectives

- Evaluate the ability of EK to deliver persulfate through clay
- Investigate the ability of low-temperature electrical resistance heating (ERH) to thermally activate persulfate
- Assess the EK-TAP concept at the field scale and its ability to degrade chlorinated ethanes and ethenes

EK-Enhanced Persulfate Migration

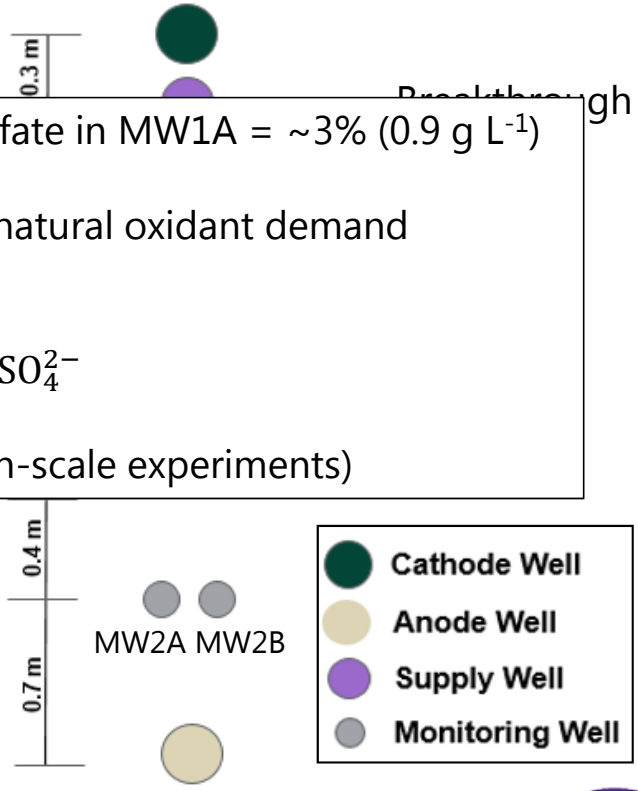
Sulfur, Sulfate, and Persulfate Groundwater Results



- Maximum concentration breakthrough of persulfate in MW1A = ~3% (0.9 g L^{-1})
- Large decomposition of persulfate likely due to natural oxidant demand
  - Fe_{total} = 6-31 g kg^{-1}

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

- Further investigation being completed (i.e., batch-scale experiments)



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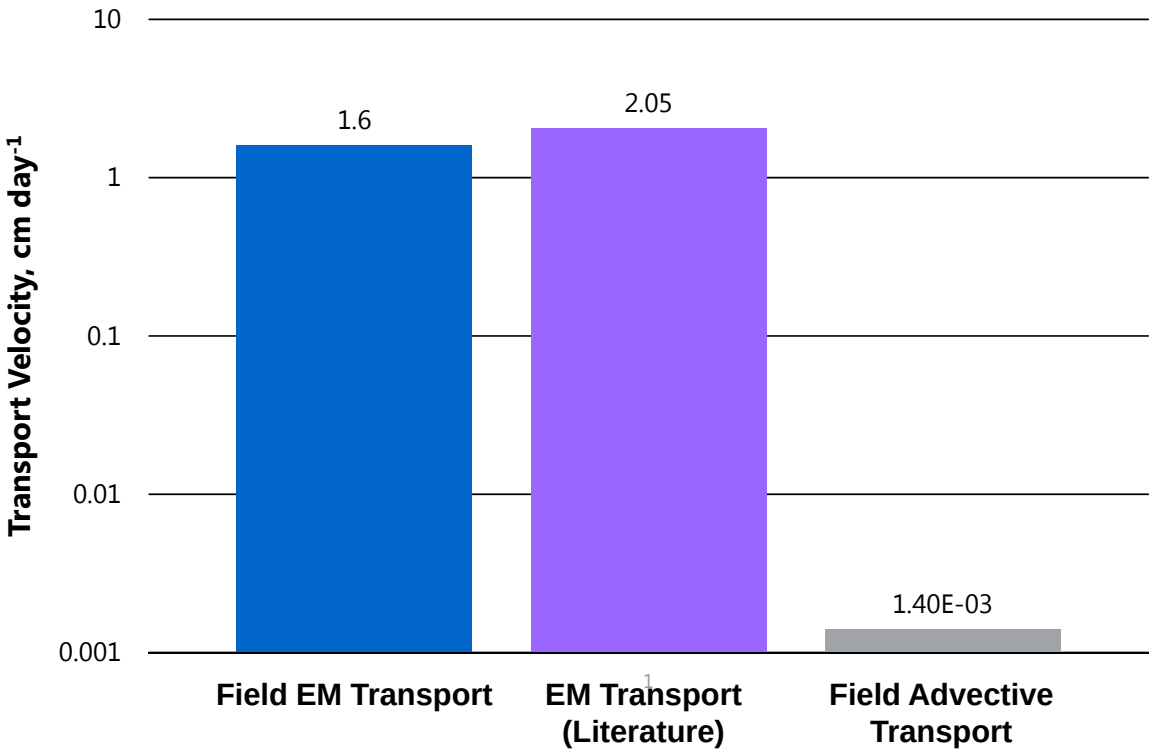
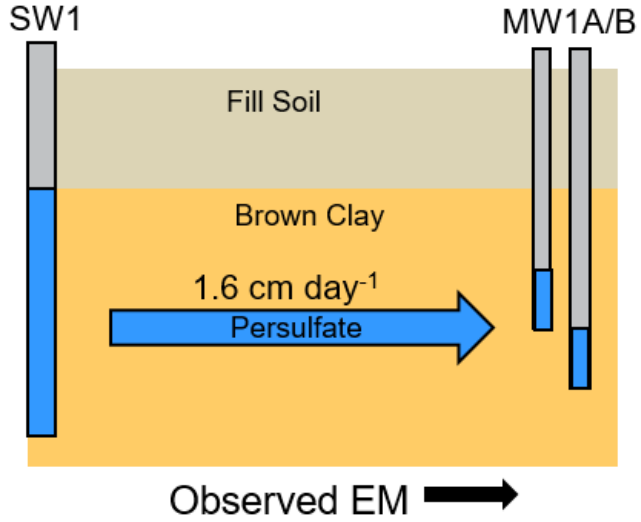
EK-Enhanced Persulfate Migration

Observed Transport Rates





$J_{EM} = U_i C_i i_e$ Effective Ionic Mobility (U_i), Concentration (C_i), Voltage Gradient (i_e)

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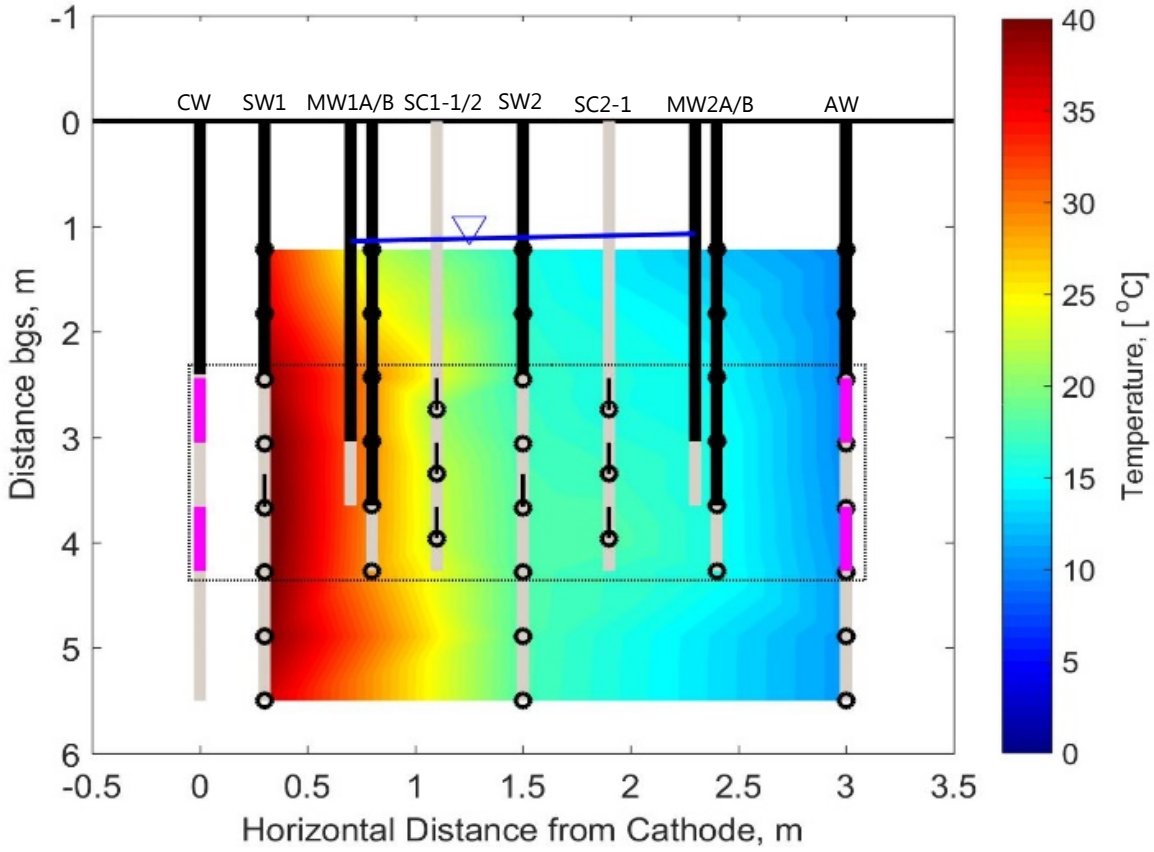
Thermal Activation of Persulfate

Low-Temperature Electrical Resistance Heating (ERH)



$$S_2O_8^{2-} \xrightarrow{Heat.} 2SO_4^{\bullet-}$$

- **ERH:** alternating current (AC) applied for 139 days
- Target temperature (30-35°C) achieved from CW to MW1A/B
- More uniform distribution in heat required

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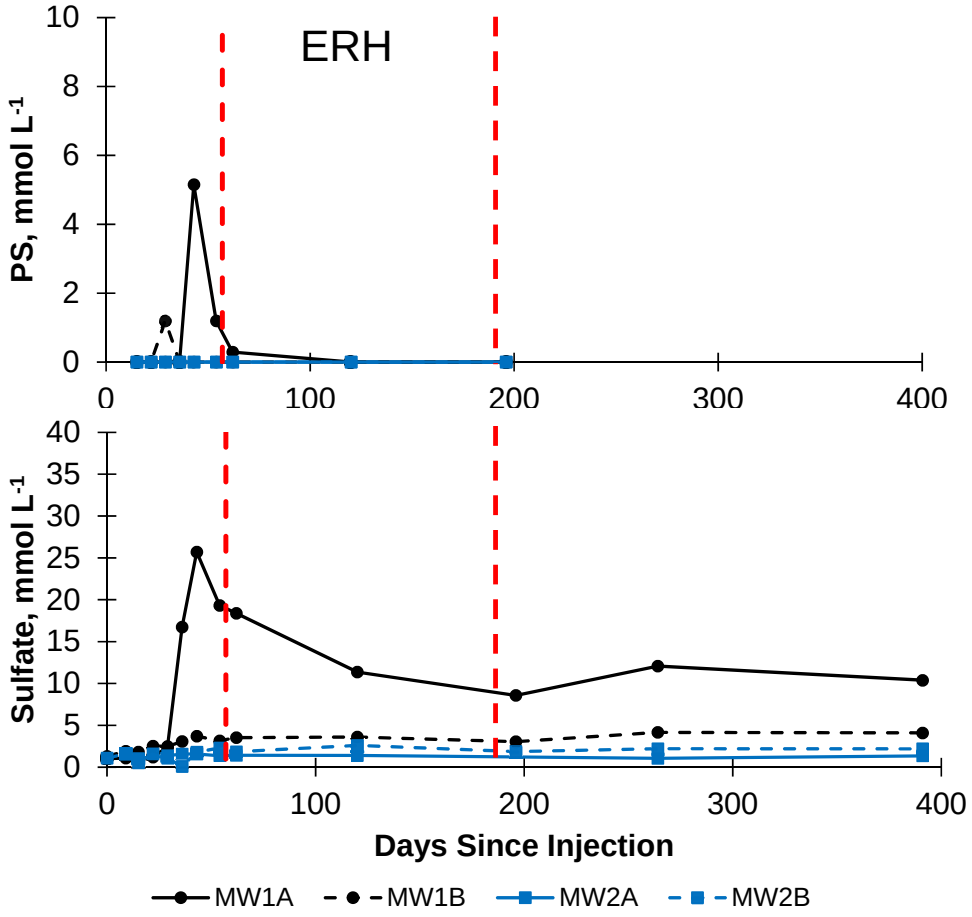
Thermal Activation of Persulfate

Low-Temperature Electrical Resistance Heating (ERH)



$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \rightarrow 2SO_4^{2-}$$

- No thermal activation assumed due to:
  - Persulfate decomposition by naturally occurring iron
  - Production of sulfate prior to ERH
  - No available persulfate during ERH for thermal activation

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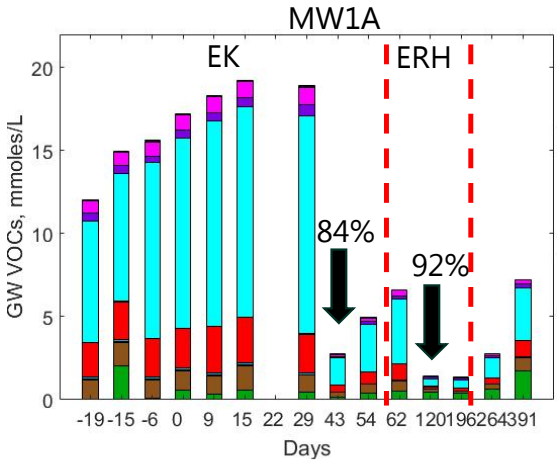
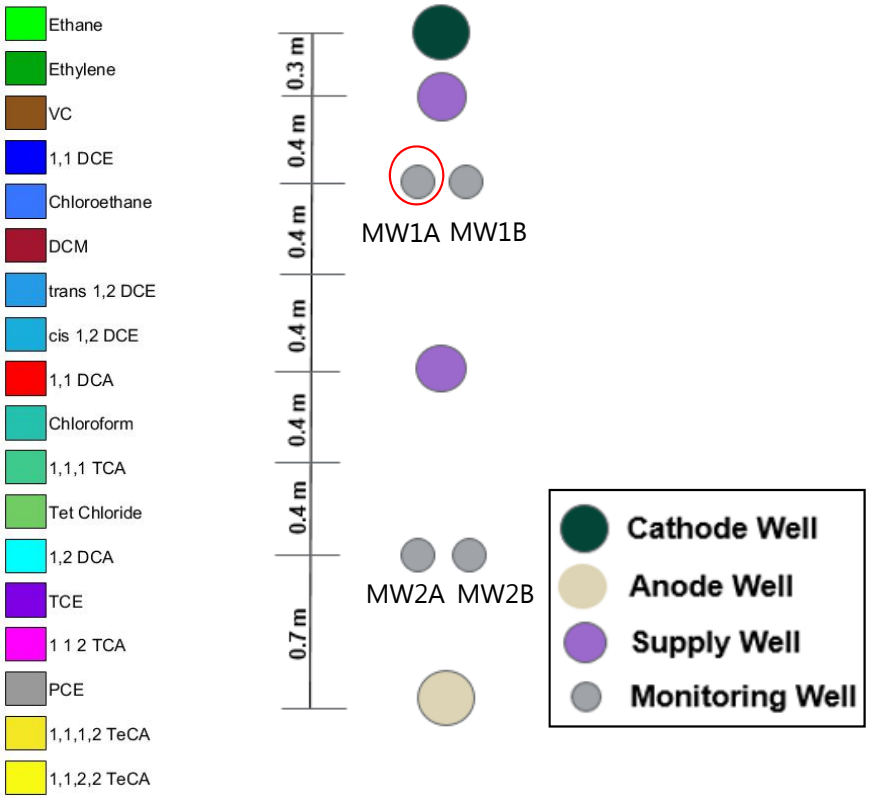
Groundwater cVOCs





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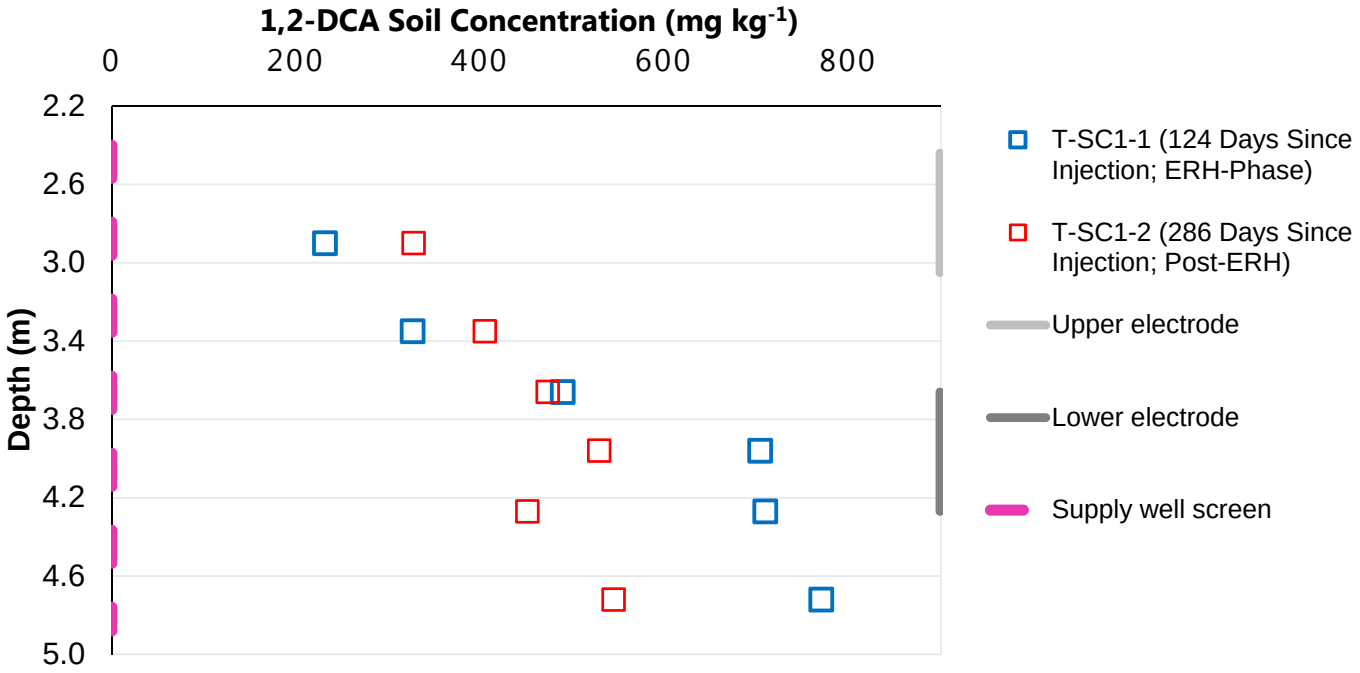
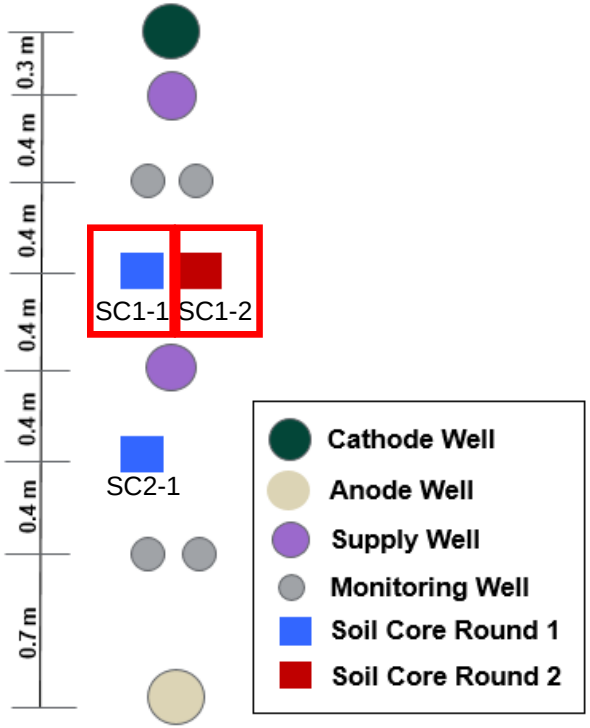
Soil cVOCs





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Conclusions

- Effective persulfate migration in clayey soil under EK-enhancement
- Target temperatures met in certain areas of EK-TAP during ERH
- Thermal activation likely precluded by iron activation
- Large decreases in VOCs observed from groundwater (>80%) at certain locations
- Decreases in VOCs observed from soil (<20%) at certain depths

Acknowledgements

Questions

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