Can PHC-Impacted Fractured Limestone Be Remediated Using ISCO?

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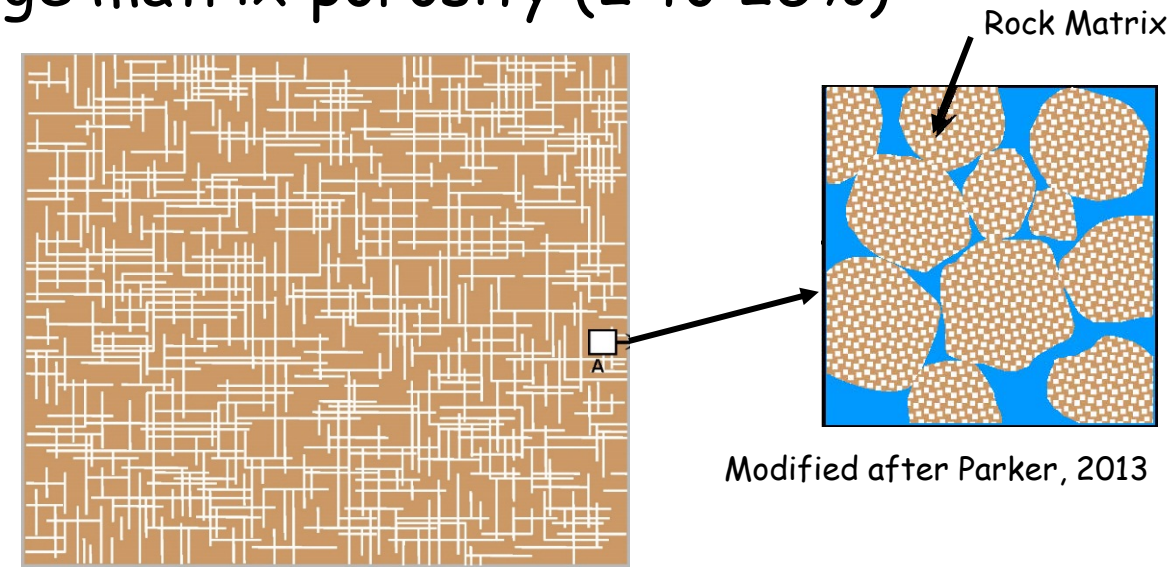
RemTech 2014 Symposium
Banff, Alberta

Background

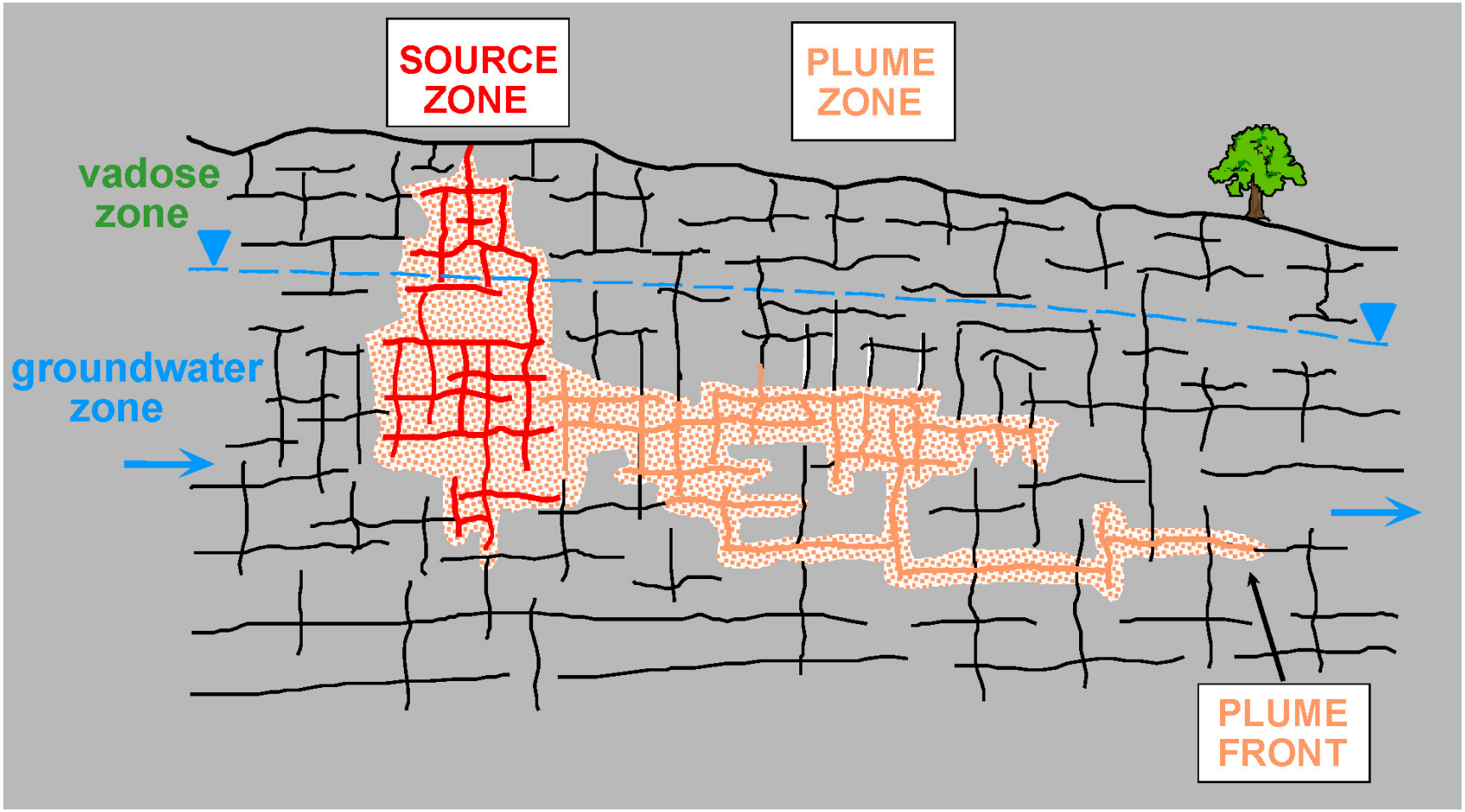
- Remediation of groundwater in fractured rock has proved problematic
  - Mackay & Cherry 1989
  - Parker et al., 2010
- Fractured Rock
  - Small fracture porosity (0.1 to 0.001%)
  - Large matrix porosity (2 to 25%)



Modified after Parker, 2013

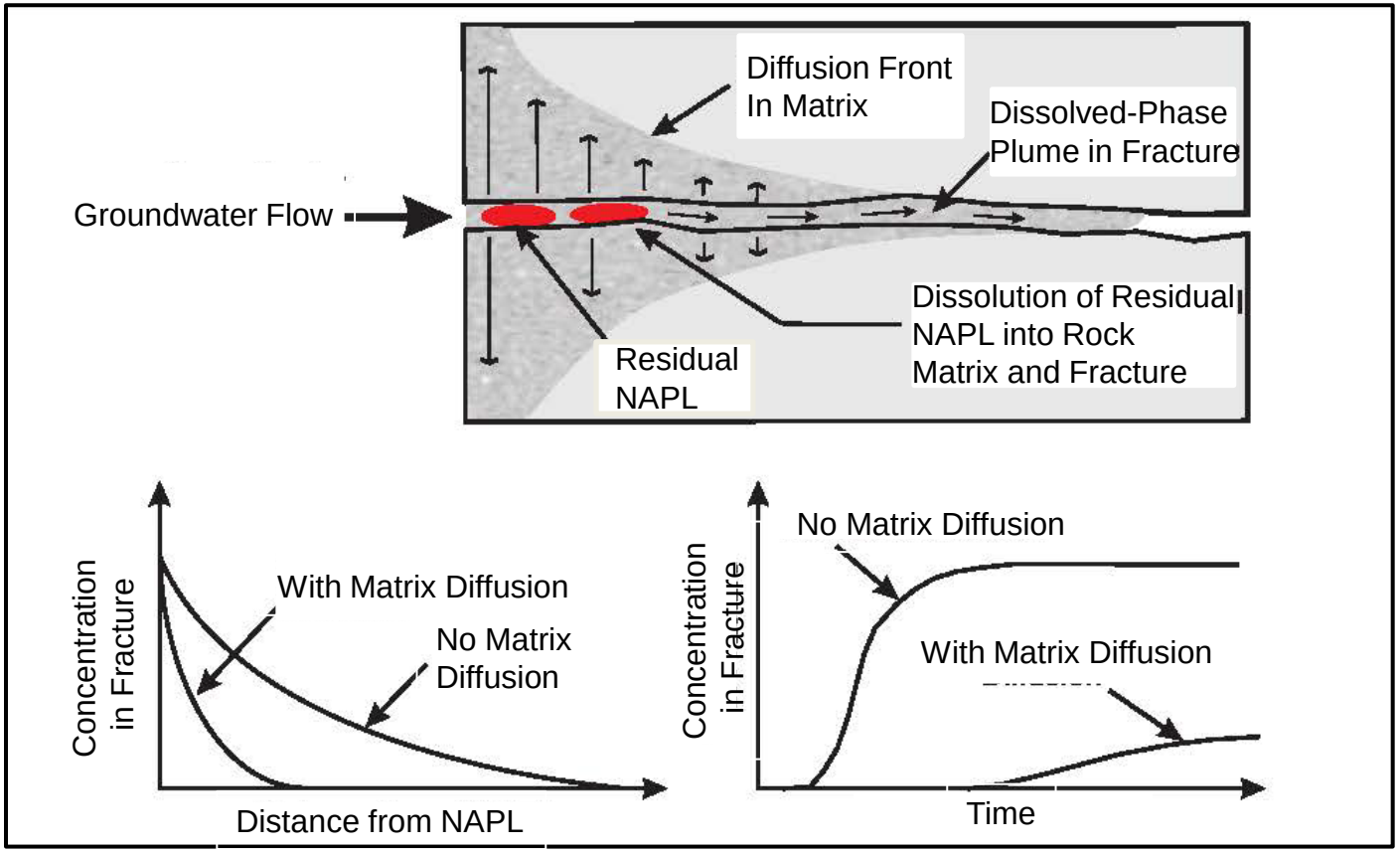
Background

- Requires integrated approaches



Modified after Parker, 2013

Background



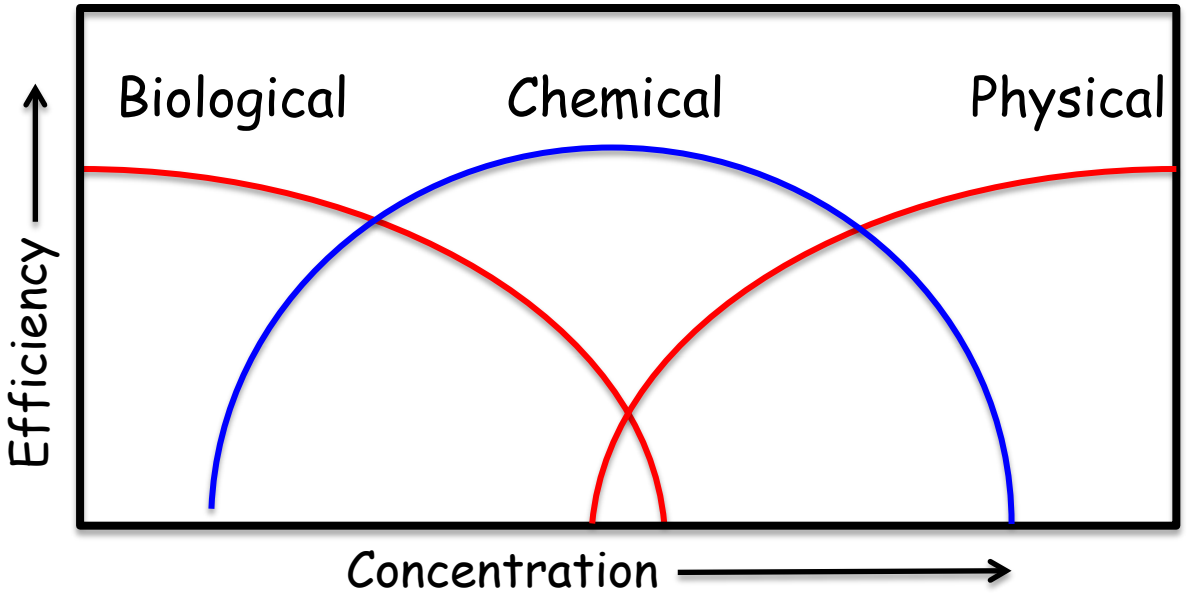
Modified after Kueper and Davies, 2009

Background

- Remediation of groundwater in fractured rock is governed by diffusion out of rock matrix (i.e. back diffusion)
- Rate of diffusion governed by:
  - Concentration
  - Time
  - Porosity
  - Organic carbon
  - Biological reactions
  - Redox species, etc.

Background

- How do we attempt to address remediation in fractured rock
- Integrated approach:
  - Combination of technologies
  - Reduction of mass
  - Increase biomass

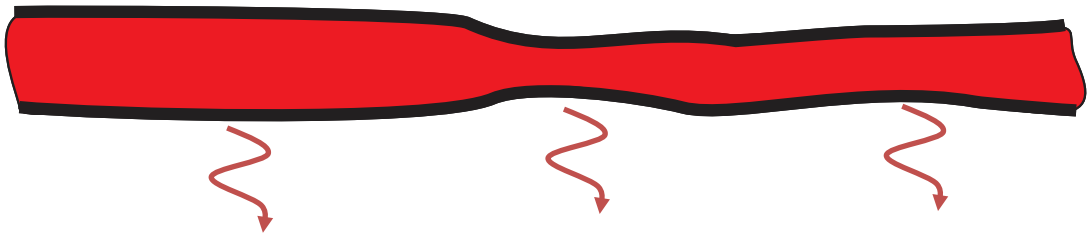


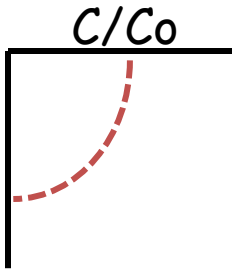
Background

- How do we attempt to address remediation in fractured rock
- Integrated approach:
  - Combination of technologies
  - Reduction of mass
  - Increase biomass
  - **Create a diffusion "reactive front"**

Background

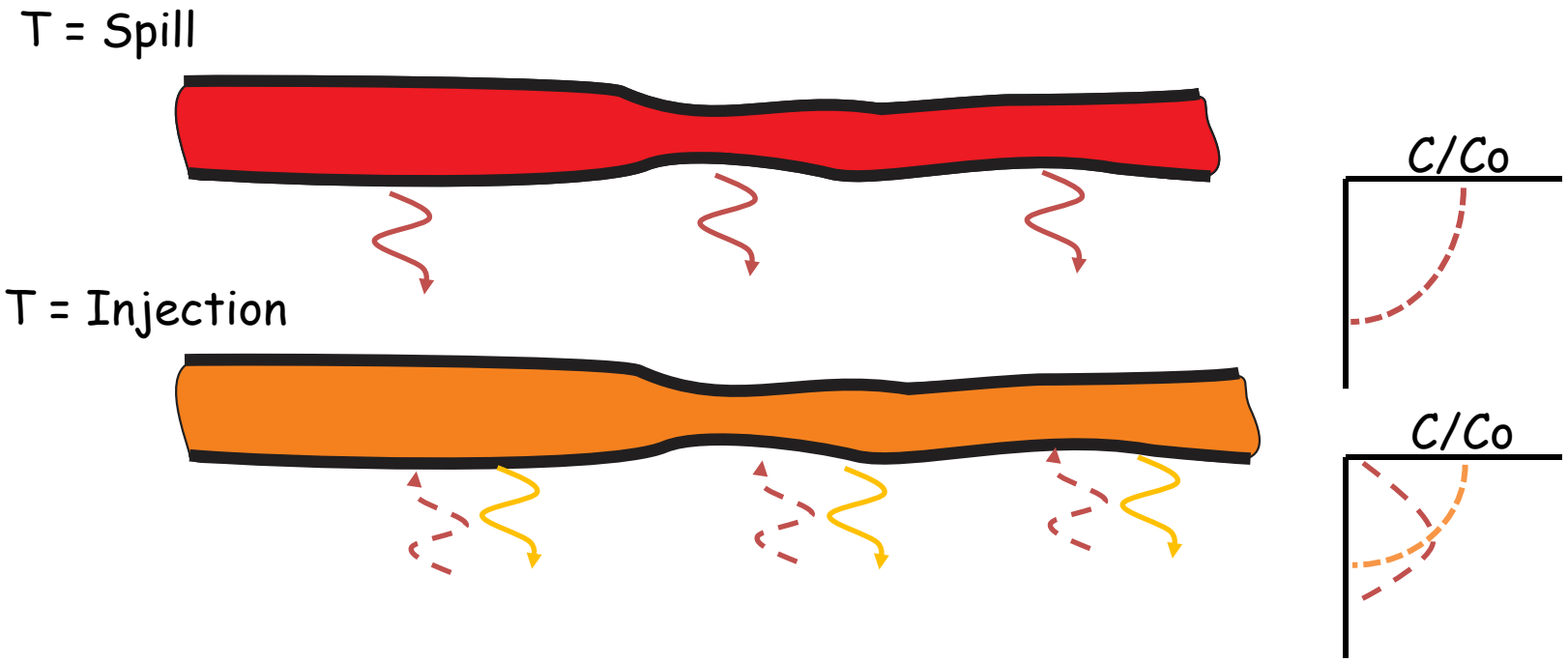
T = Spill



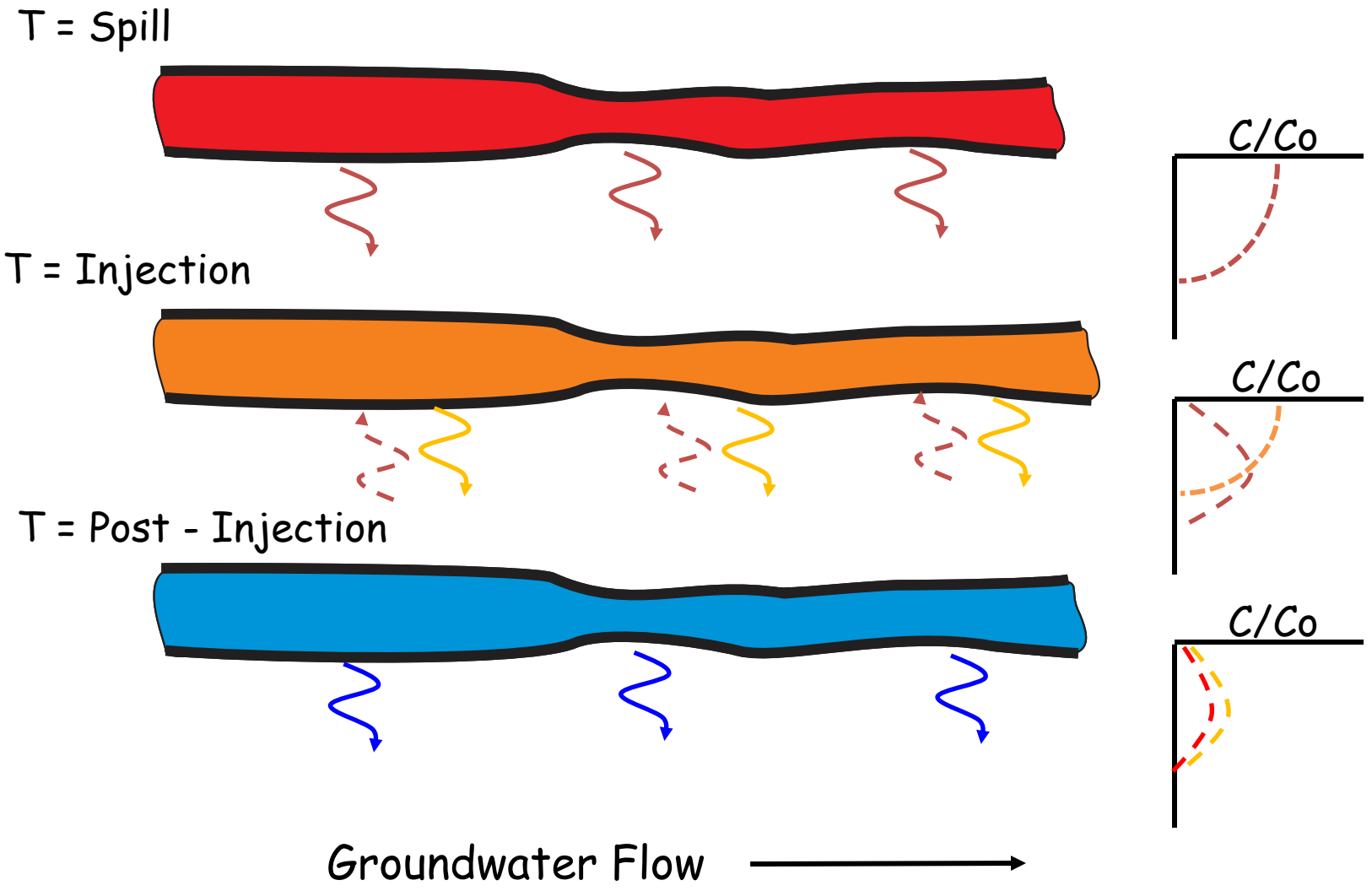


Groundwater Flow →

Background



Background


T = Spill
T = Injection
T = Post - Injection
C/Co
C/Co
C/Co
Groundwater Flow

Background

Persulphate Anion

$$S_2O_8 + 2H^+ + 2e^- \rightarrow 2HSO_4^{-1}$$

Activation

$$SO_4^{\bullet -} + e^- \rightarrow SO_4^{-2}$$

Initiation

$$S_2O_8^{2-} \rightarrow SO_4^{\bullet -} + (SO_4^{\bullet -} \text{ or } SO_4^{-2})$$

Propagation

$$SO_4^{\bullet -} + H_2O \rightarrow OH^{\bullet -} + HSO_4^-$$

Termination

$$SO_4^{\bullet -} + RH \text{ or } M \rightarrow SO_4^{-2}$$

Background

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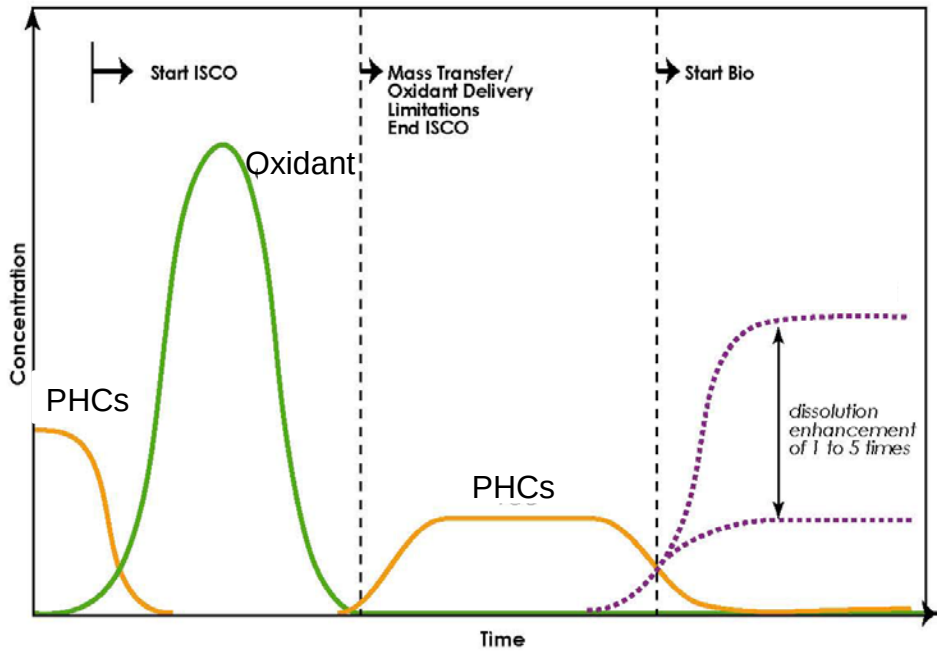
Study Site

- Remedial program
  - Excavation of overburden to limestone surface
  - Pumping of NAPL
  - ISCO of dissolved phase
  - EAB of residue



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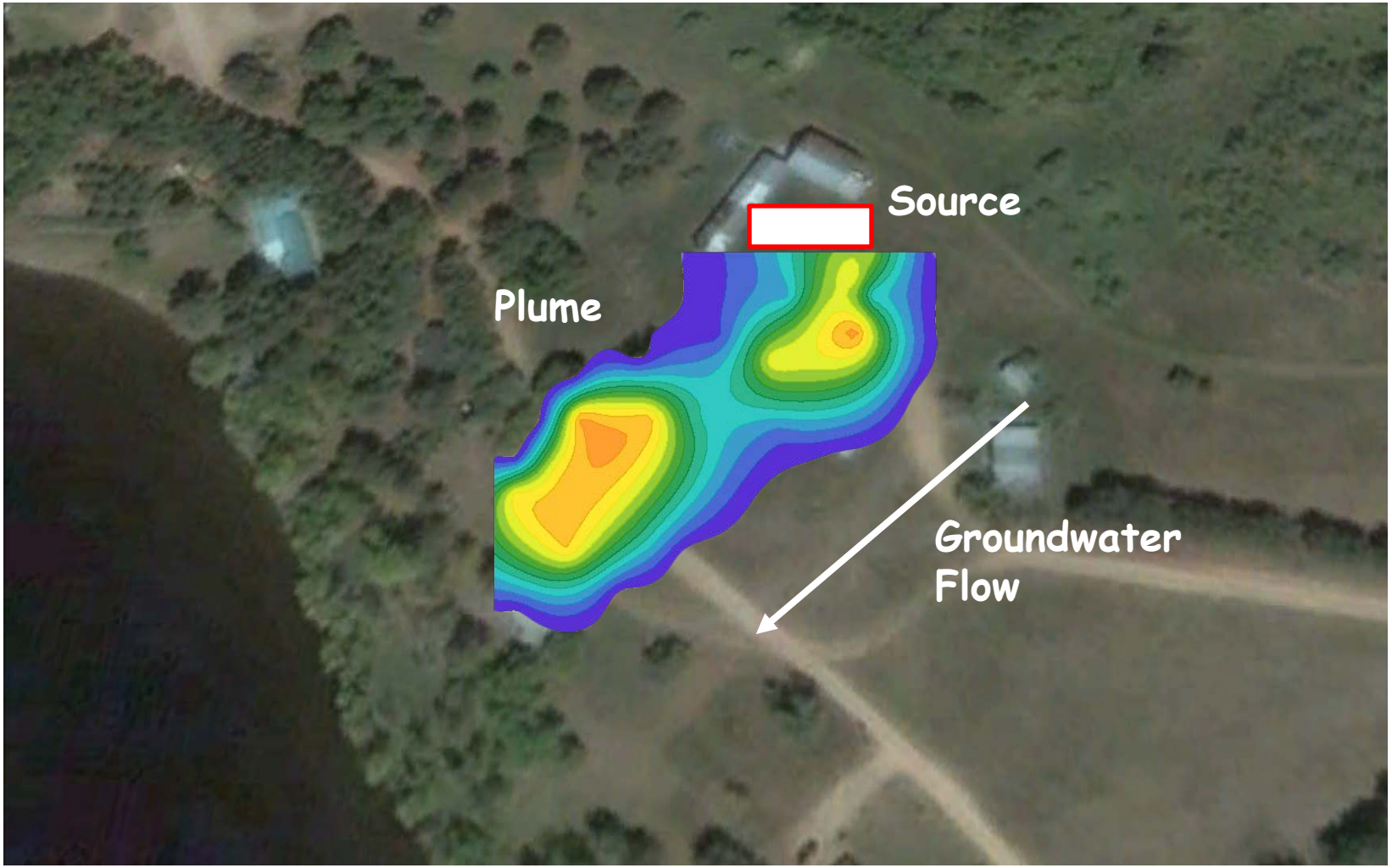
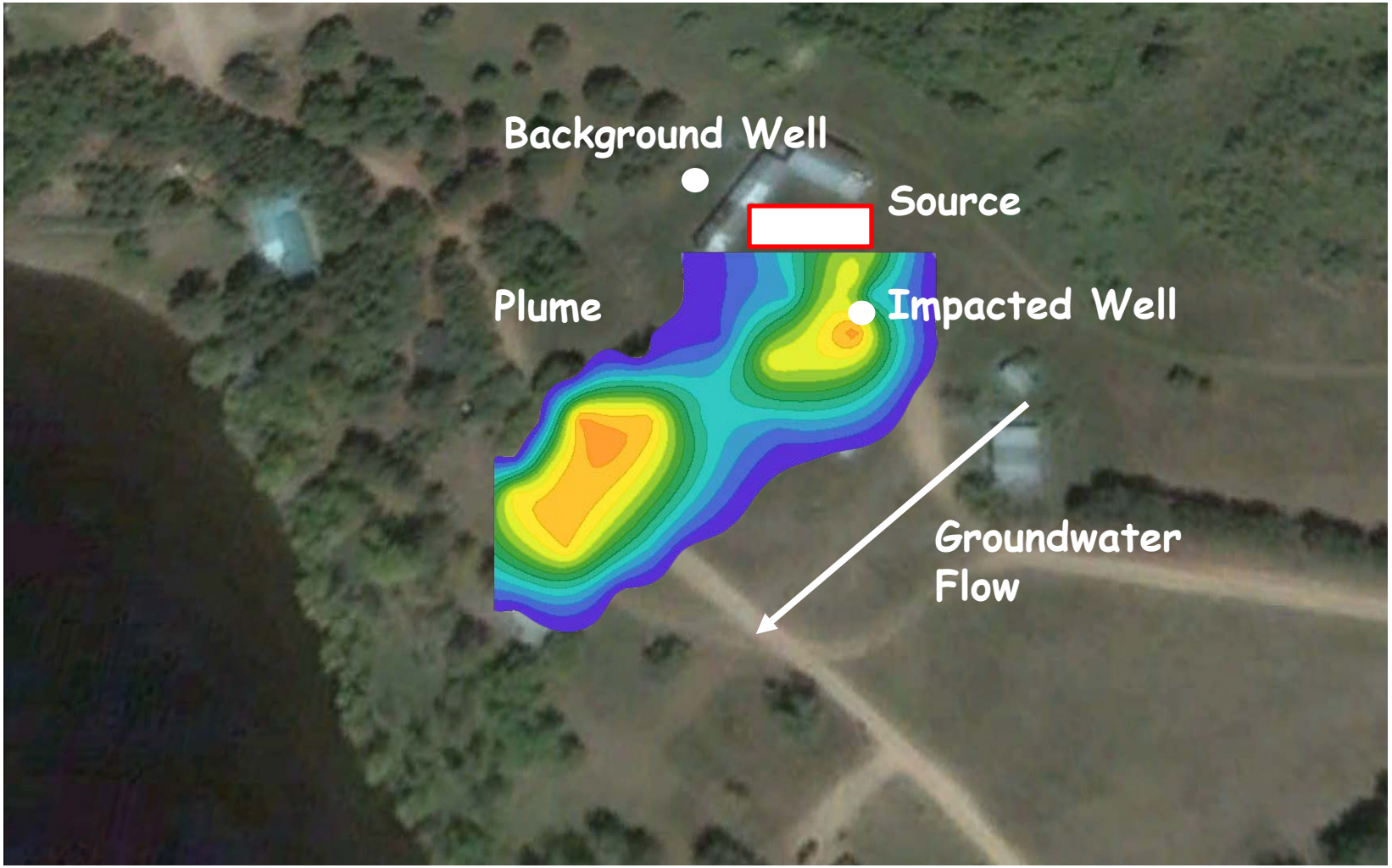
Site

- Residential site, Central Ontario
- Fuel oil spill
  - ~600 L
- Geology
  - Glacial overburden (~ 1 m thick)
  - Fractured limestone
- Hydrogeology
  - Water table within limestone
  - ~0.5 m/year fluctuation
  - Packer testing
- Geochemistry
  - Iron/sulphate reducing

PHC Plume



PHC Plume


Background Well
Source
Plume
Impacted Well
Groundwater
Flow

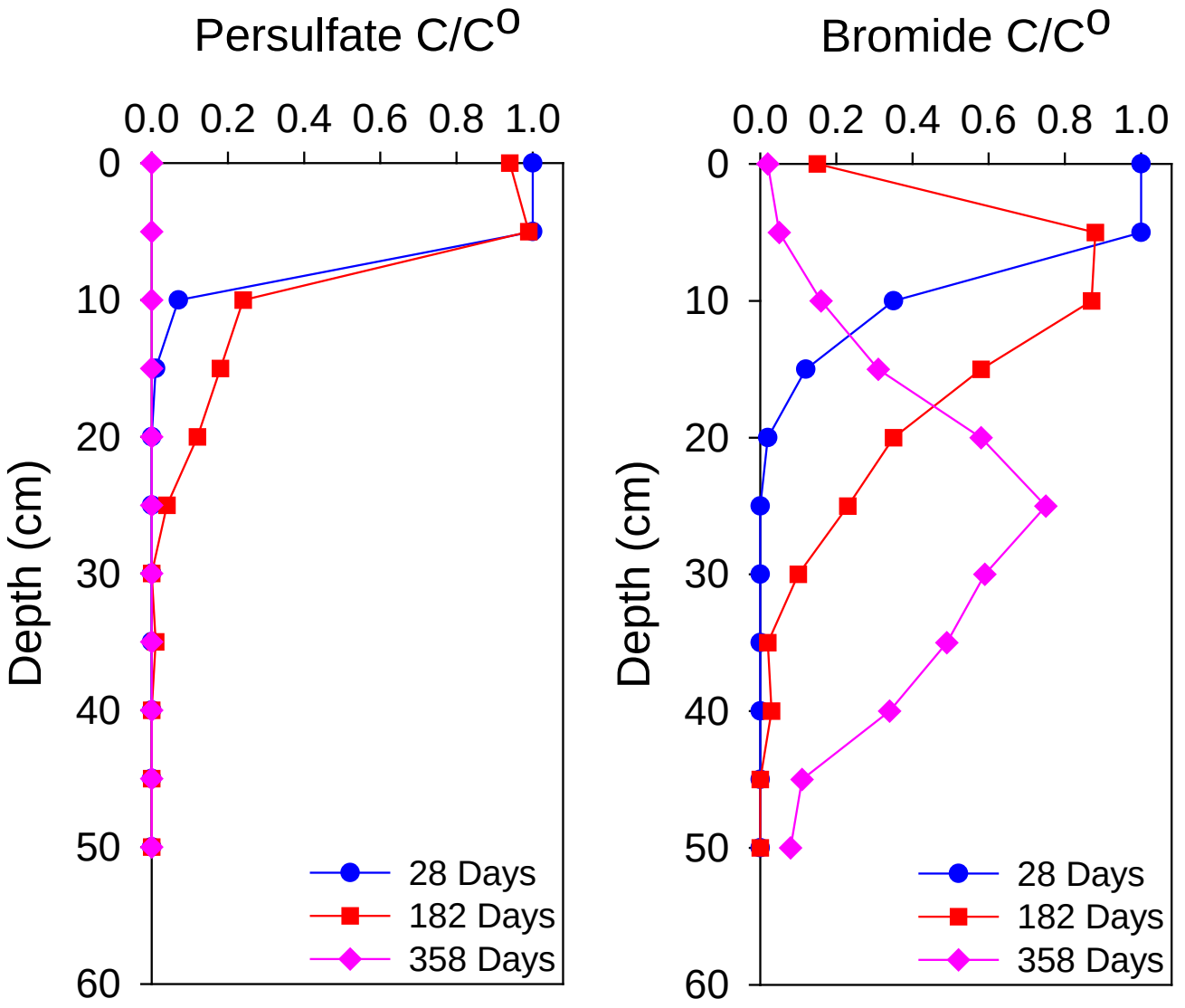
Injection Program

- Oxidant
  - Sodium persulphate activated sodium hydroxide
  - Supplemented with 100 mg/L NaBr tracer
- Injection program
  - Four injections over 6 months
  - 2 locations
    - Background & Impacted
  - Injections completed using packers
    - 15 wt.% S_2O_8
    - 20 psi
    - 650 L/well per injection

Monitoring Program

- Cores of rock collected
  - Pre injection
  - 1, 6 & 12 months after last injection event
  - Frozen on site
  - Sampled in lab at 5 cm intervals
  - Analysis
    - Persulphate,
    - Bromide and
    - pH

Non-Impacted Fracture Profiles



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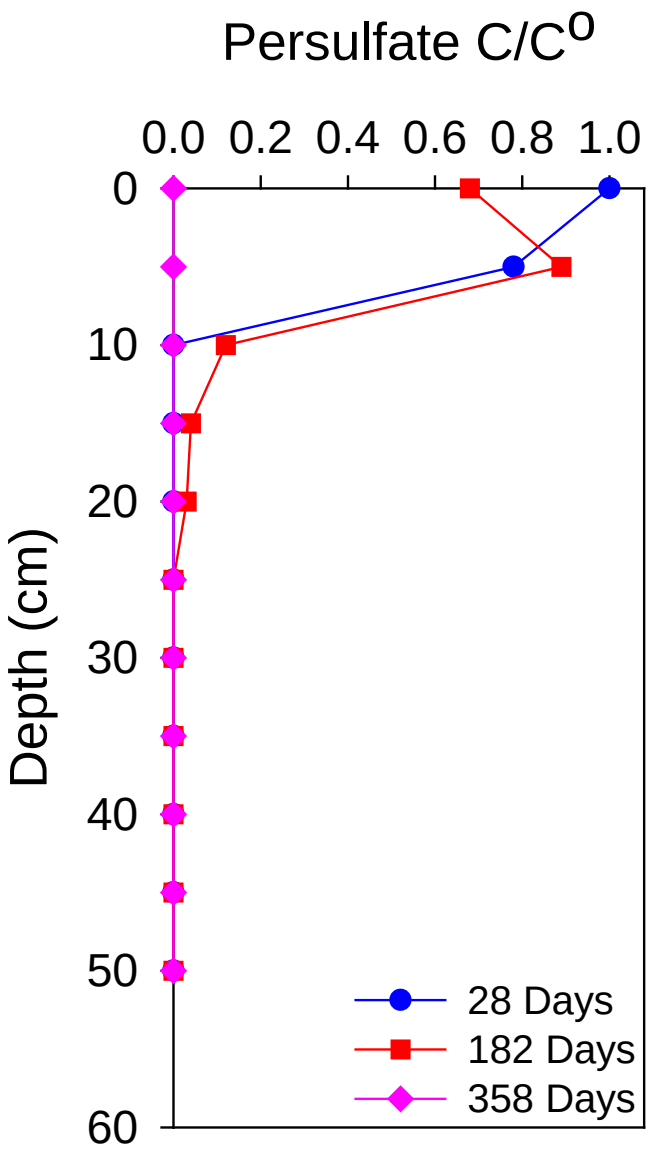
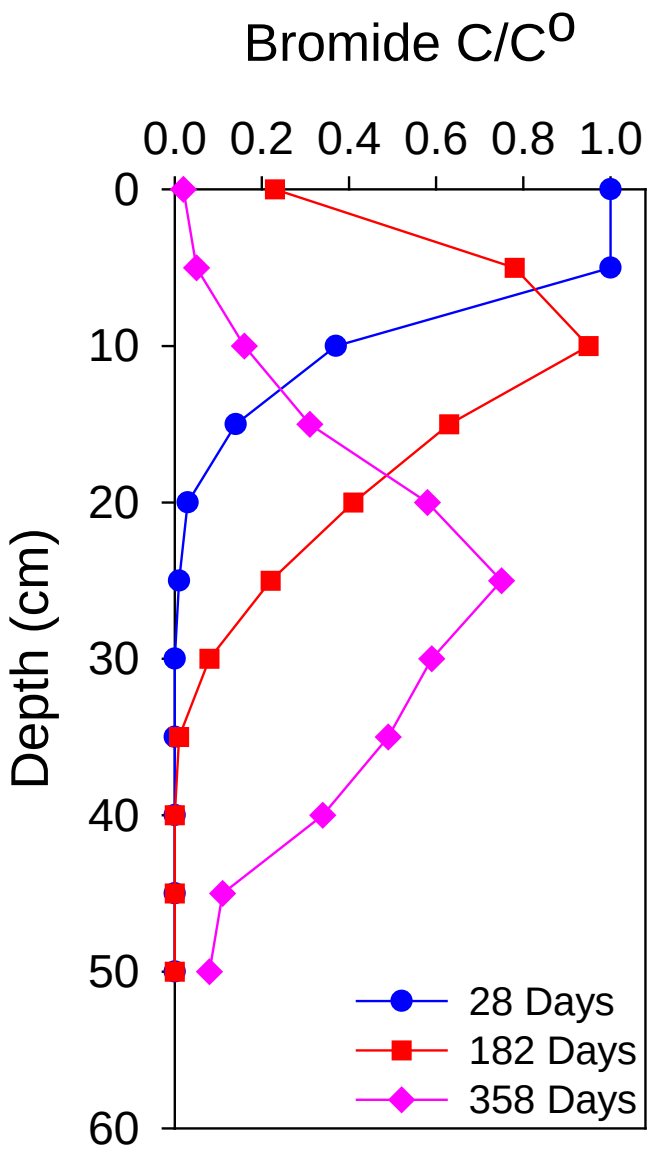
PHC-Impacted Fracture Profiles





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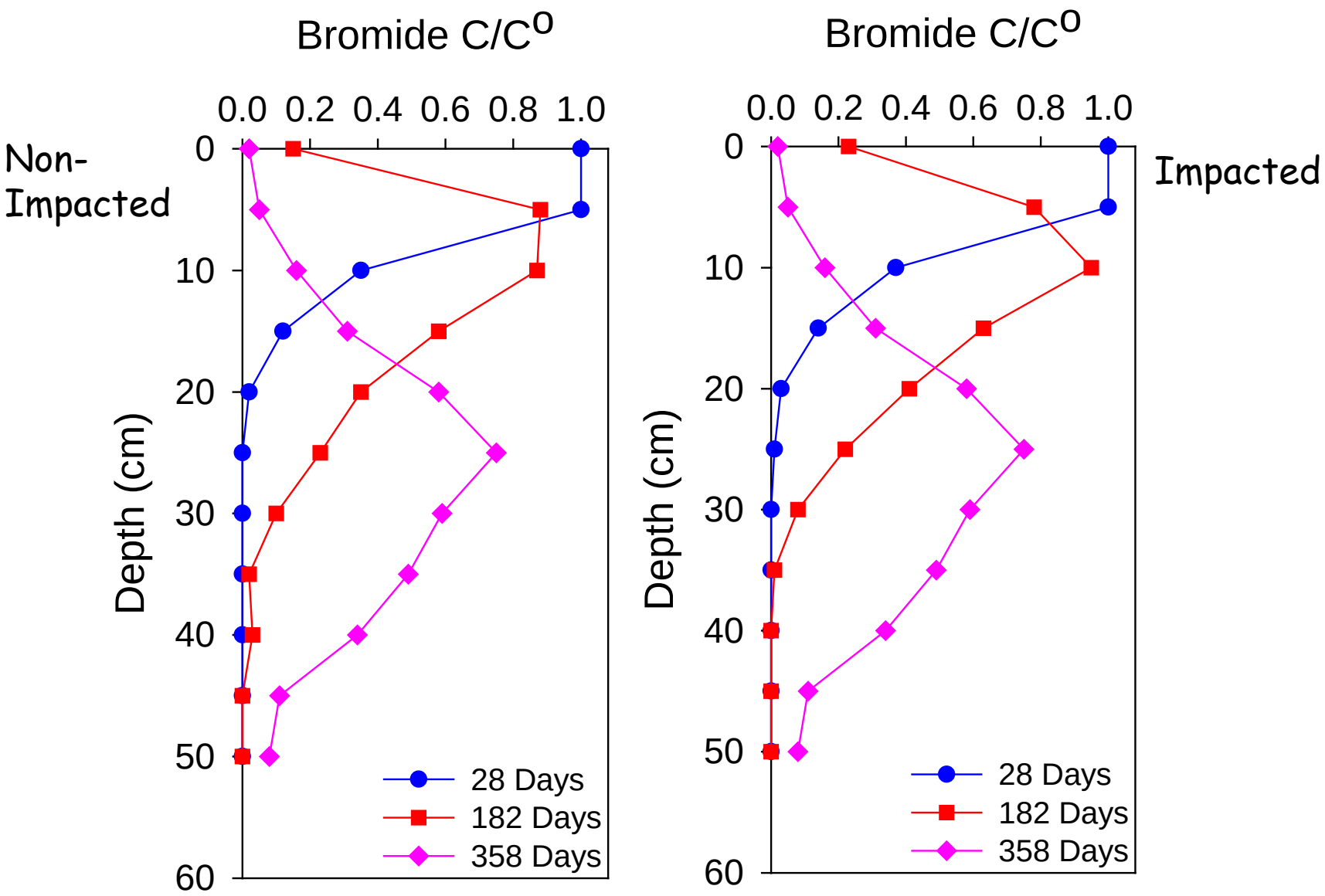
Bromide Profiles



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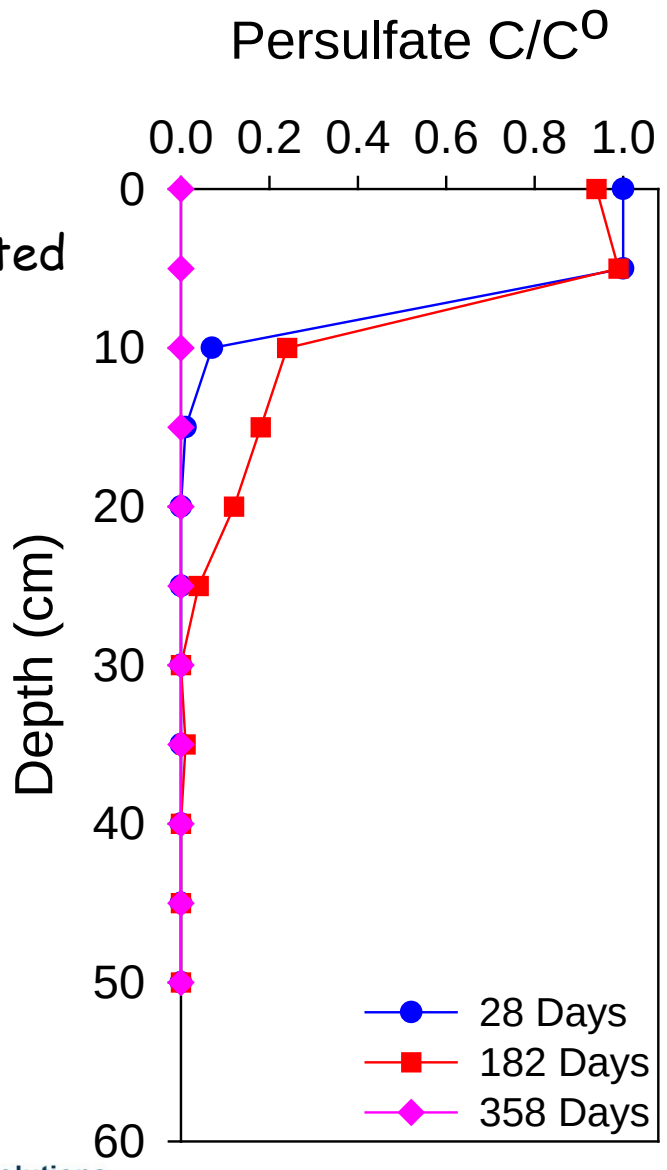
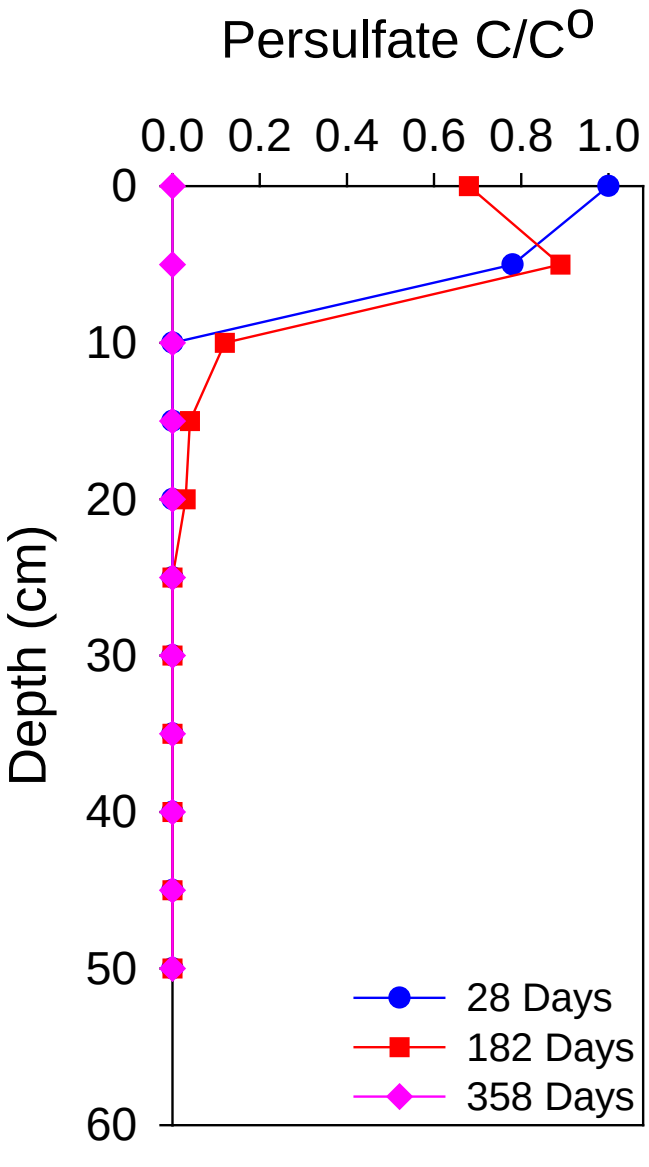
Persulphate Profiles

Non-Impacted





Impacted

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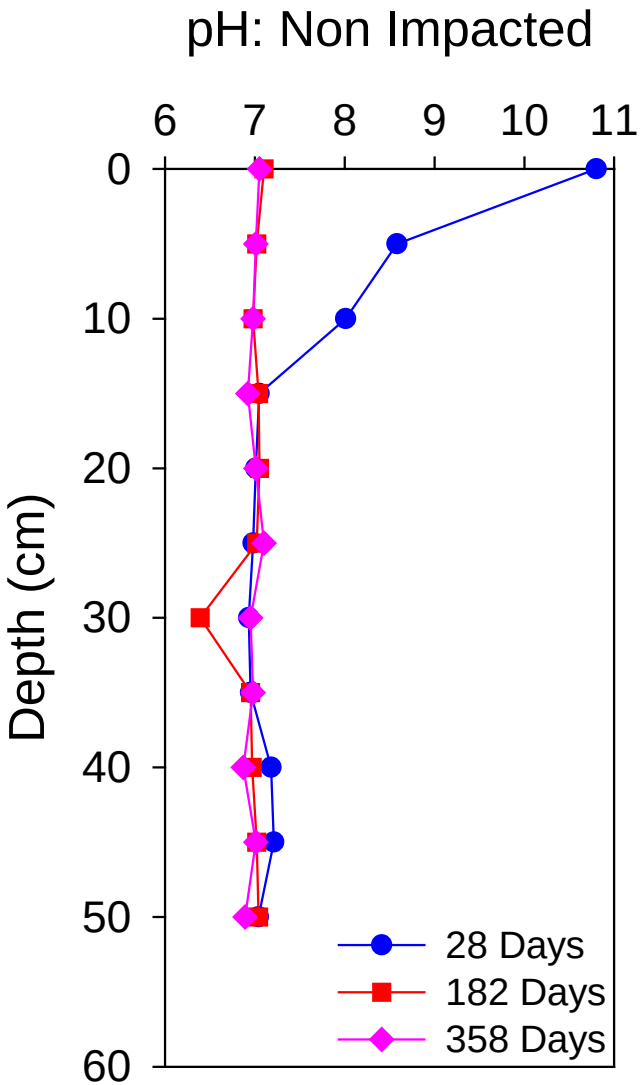
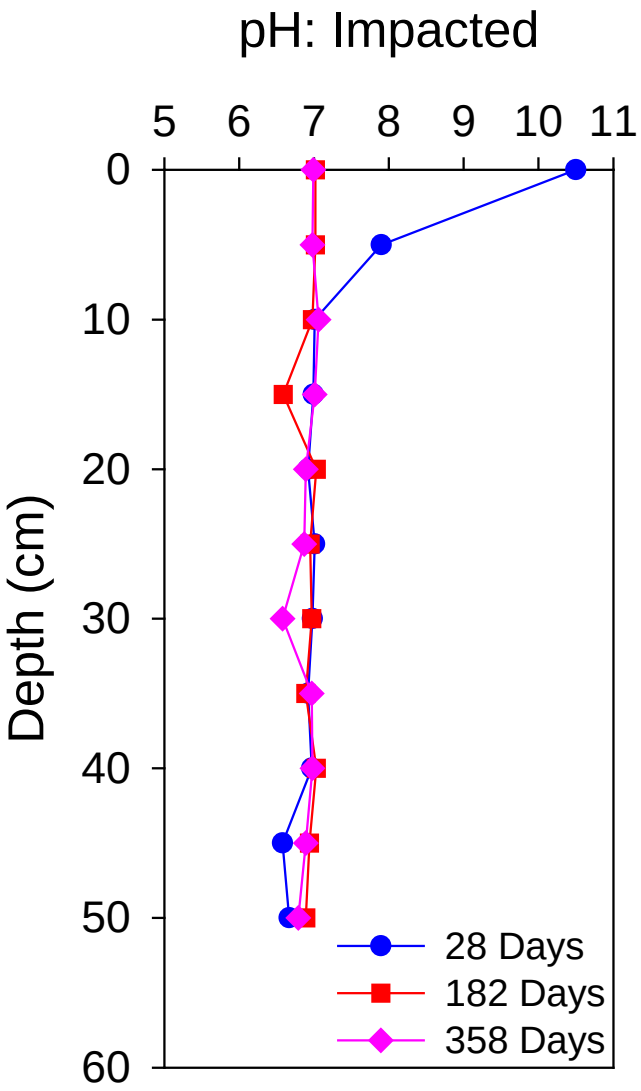
pH Profiles





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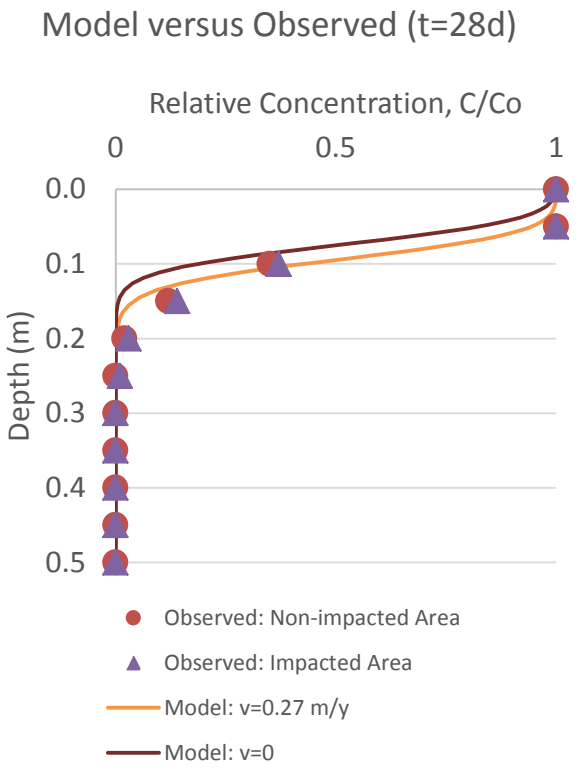
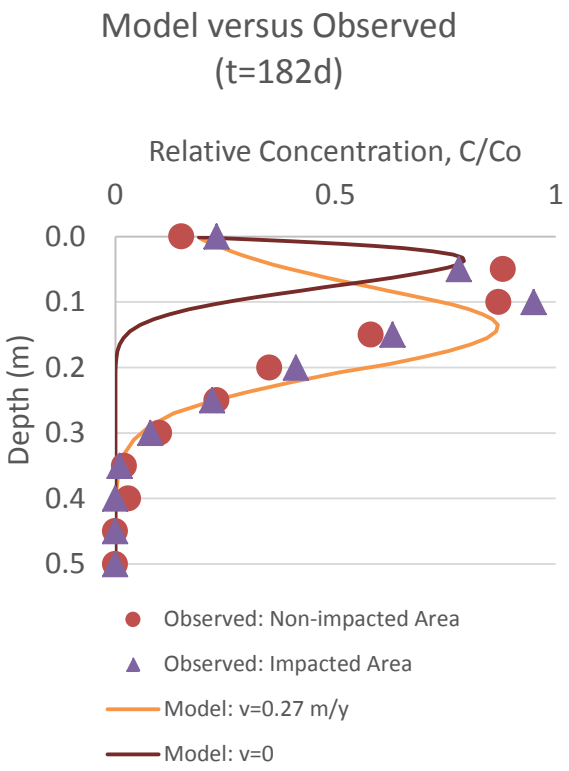
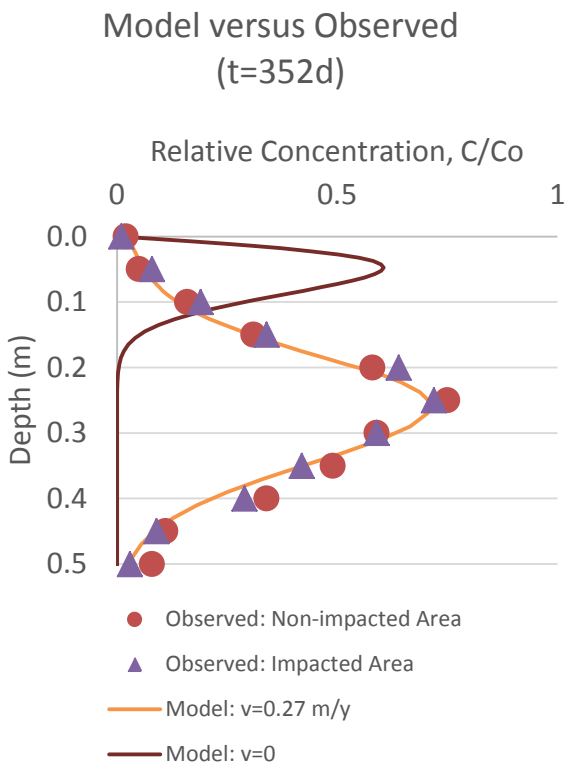
Model

- BioRedox-MT3DMS
  - Van Genuchten analytical solution
  - 3 D
  - 1 D simulations
  - Calibration based on Merkel (2010)
    - ESTCP diffusion column
    - Compared with Sra (2010)
  - Bromide degradation negligible
  - Persulphate half lives between 25 & 50 days

Bromide Calibration





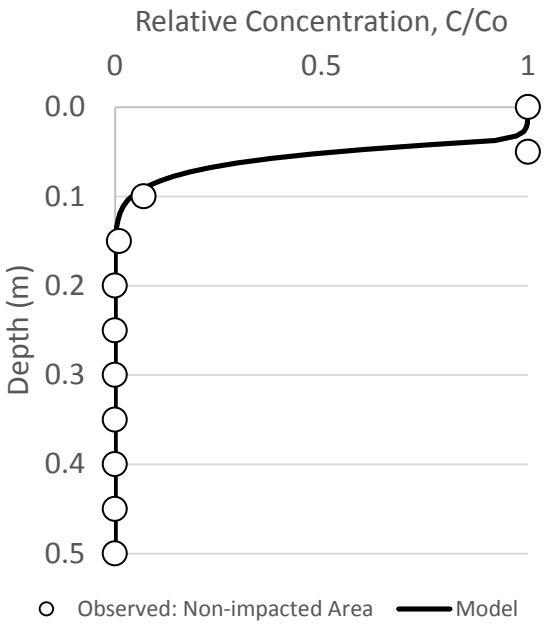


Data for t= 182 days suggests that a downward velocity continued after injection

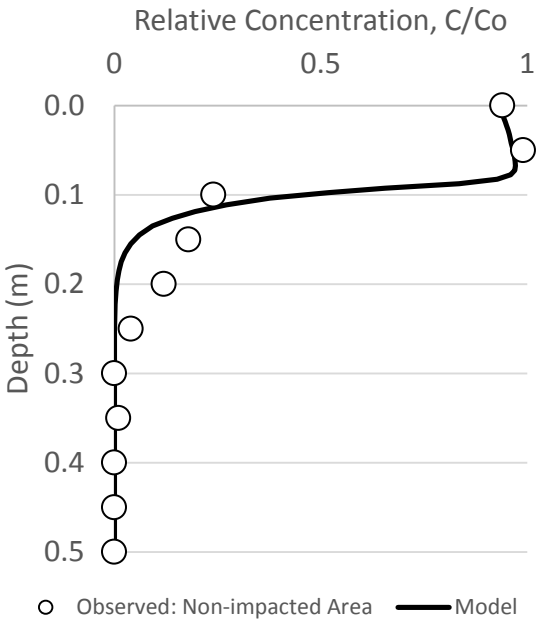
Persulphate Simulation

Non Impacted Fracture

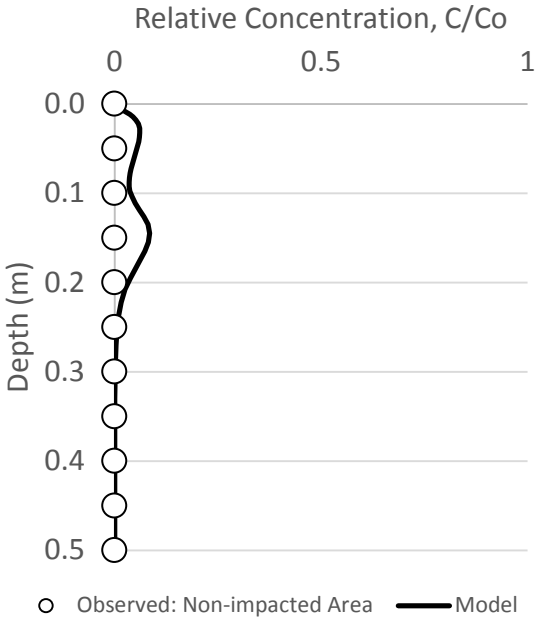
Model versus Observed
(t=28d)



Model versus Observed
(t=182d)



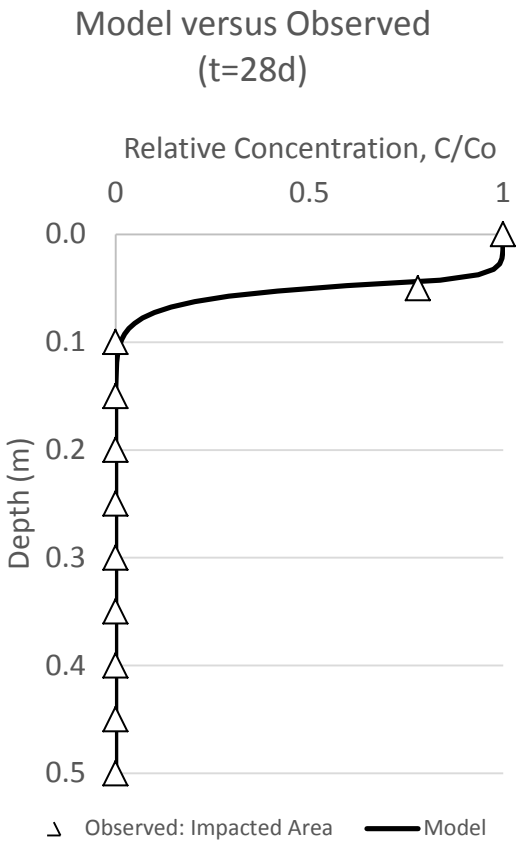
Model versus Observed
(t=352d)

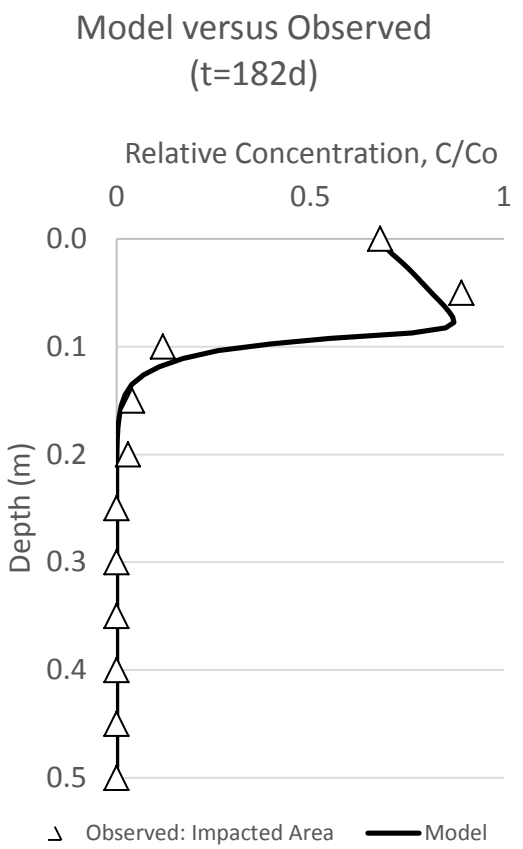


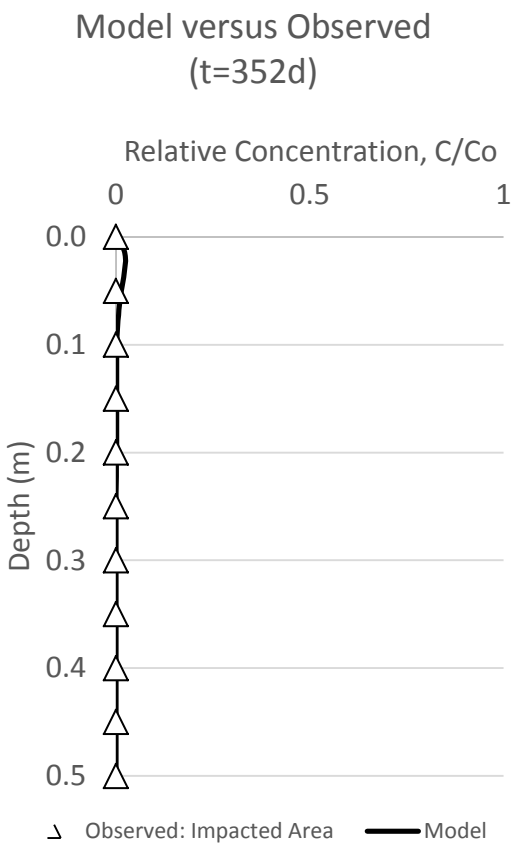
Half life is 25 days

Persulphate Simulation

PHC-Impacted Fracture







Half life is 15 days

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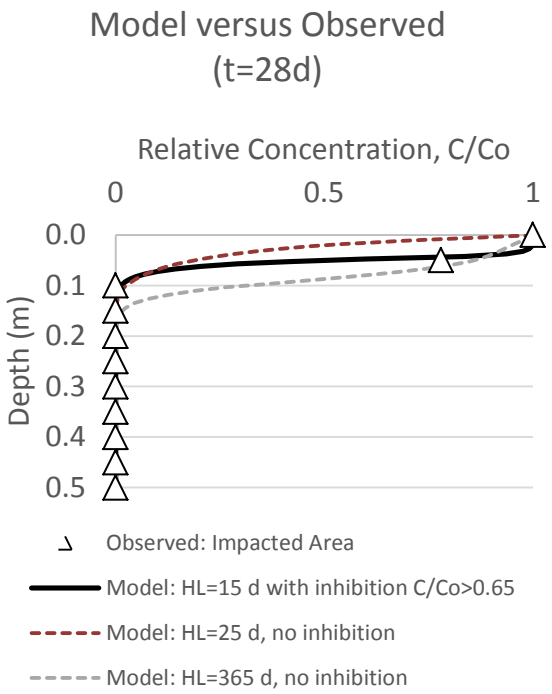
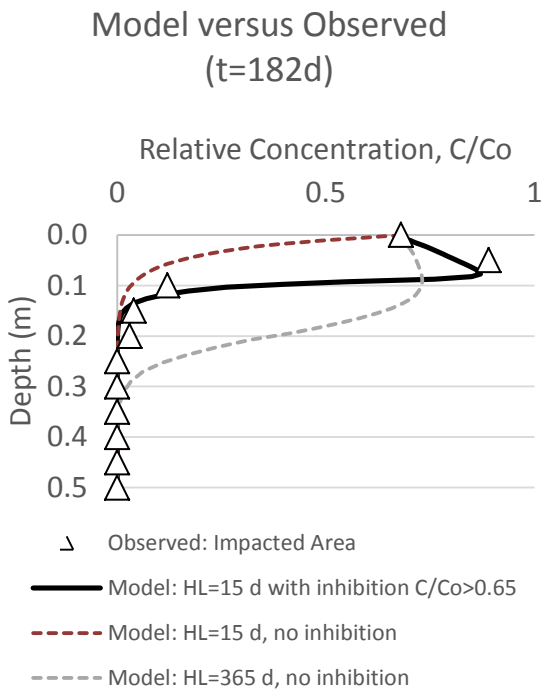
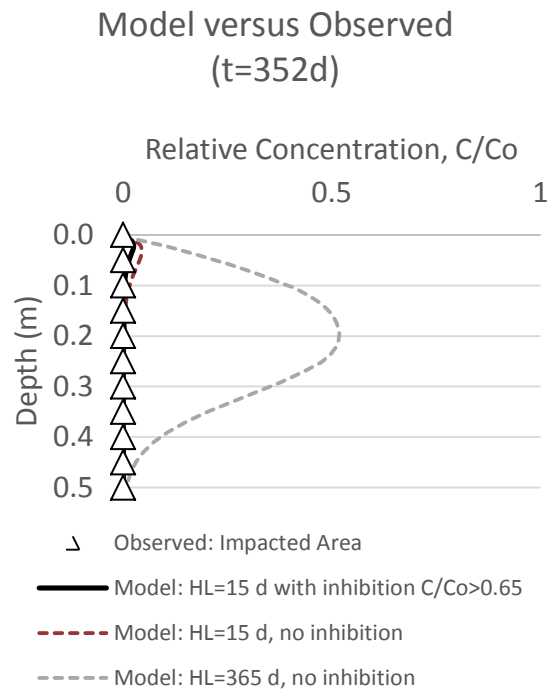
Persulphate Simulation

PHC-Impacted Fracture Sensitivity Analysis







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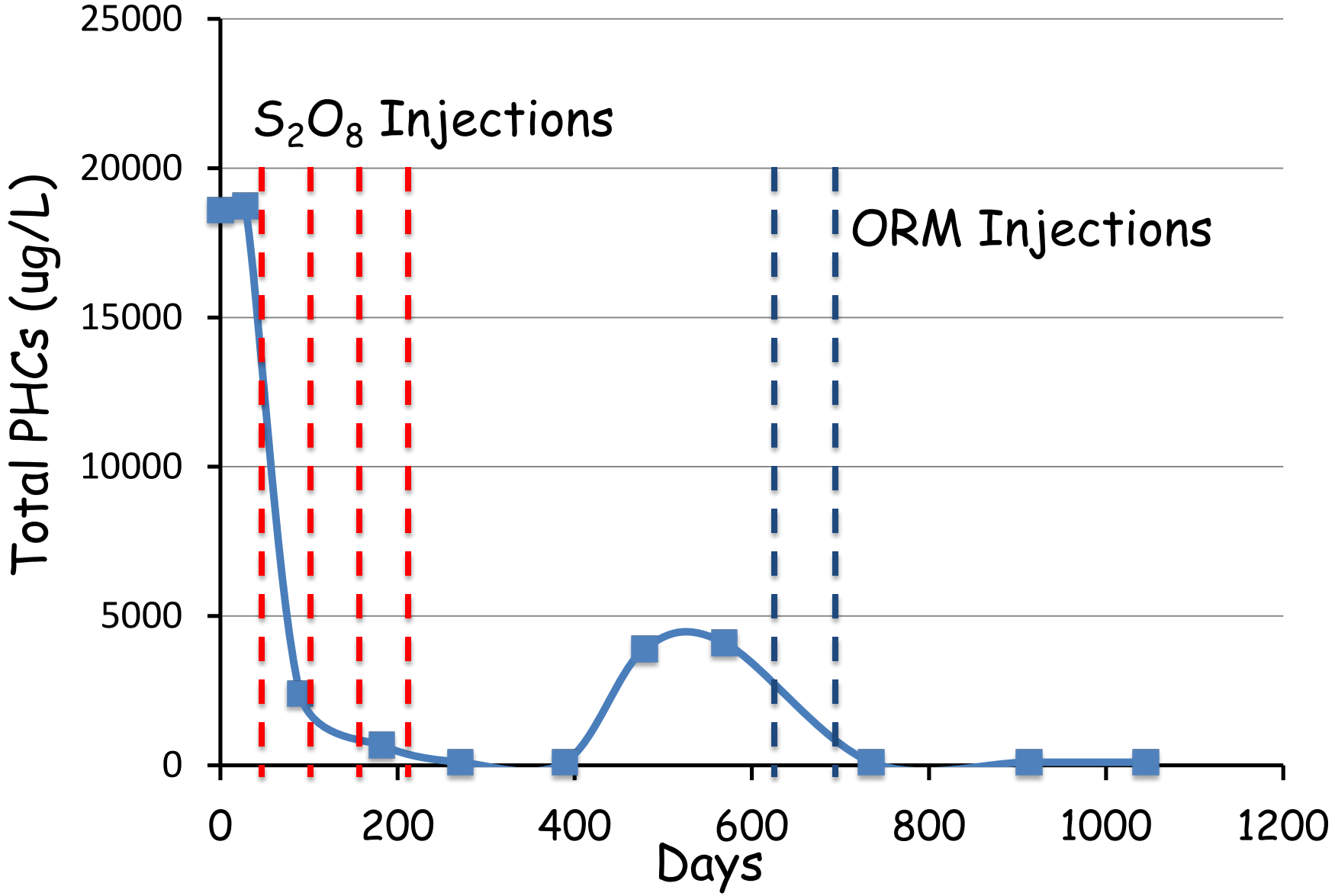
Treatment



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Observations

- Fractured rock remediation provides a special challenge due to diffusion-controlled processes
- Limited tools available to address diffusion
- Chemical oxidation tools include:
  - High concentrations
  - Persistence
  - Long term oxidant source
- Diffusion of persulphate
  - ~20 cm impacted matrix vs ~30 cm vs non-impacted matrix
- Persulphate degrades in absence of PHCS:
  - ~ 25 day half live vs 15 days in presence of PHCs
- pH activation may be issue
  - Evaluated pH (>10) observed at 10 cm for less than 3 months in both impacted and non-impacted matrices, suggesting buffering reactions are occurring

Questions