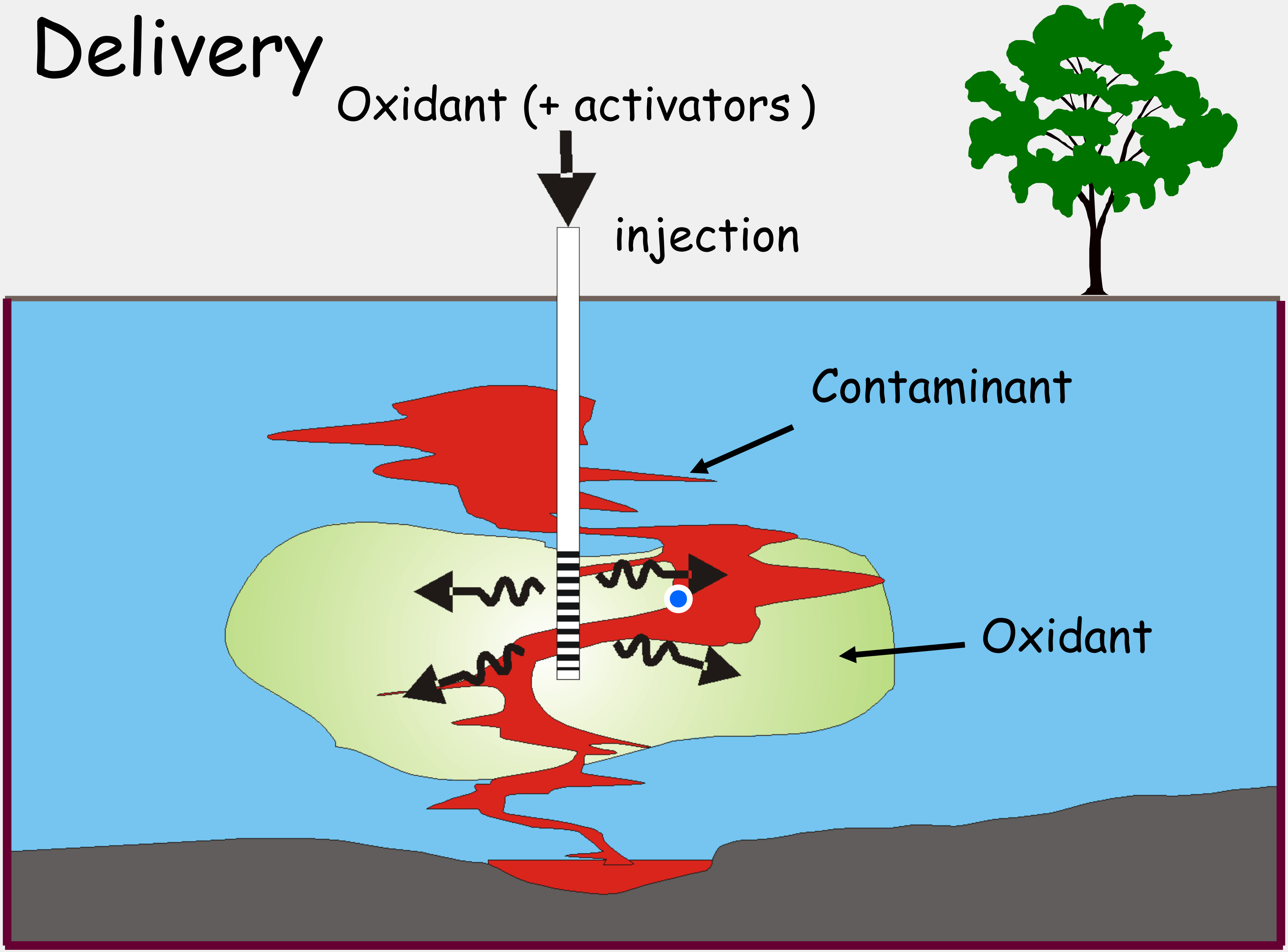
Oxidant Stability vs NOD – Comparison of Peroxide, Persulfate and Permanganate

Neil R. Thomson
Department of Civil & Environmental Engineering
University of Waterloo,
CANADA
(*nthomson@uwaterloo.ca*)

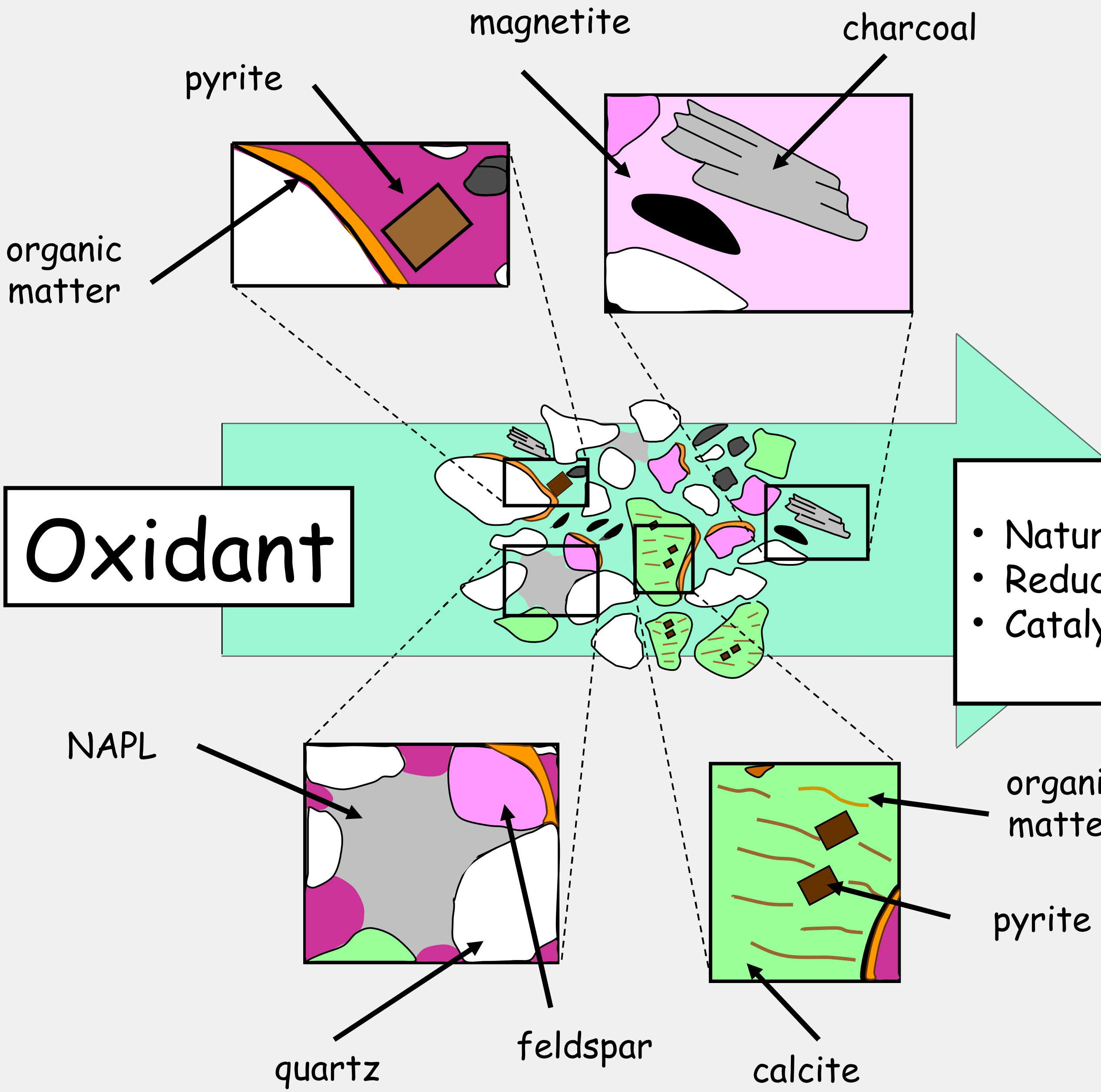
University of Waterloo

Waterloo FACULTY OF ENGINEERING

Delivery



Pore Scale Conceptual Model



- Natural Organic Matter (NOM)
- Reduced Inorganics (Fe, Mn, etc)
- Catalyses

Adapted from Mumford, Thomson, and Allen-King, ES&T, 2005.

Treatment Implications

Increase…

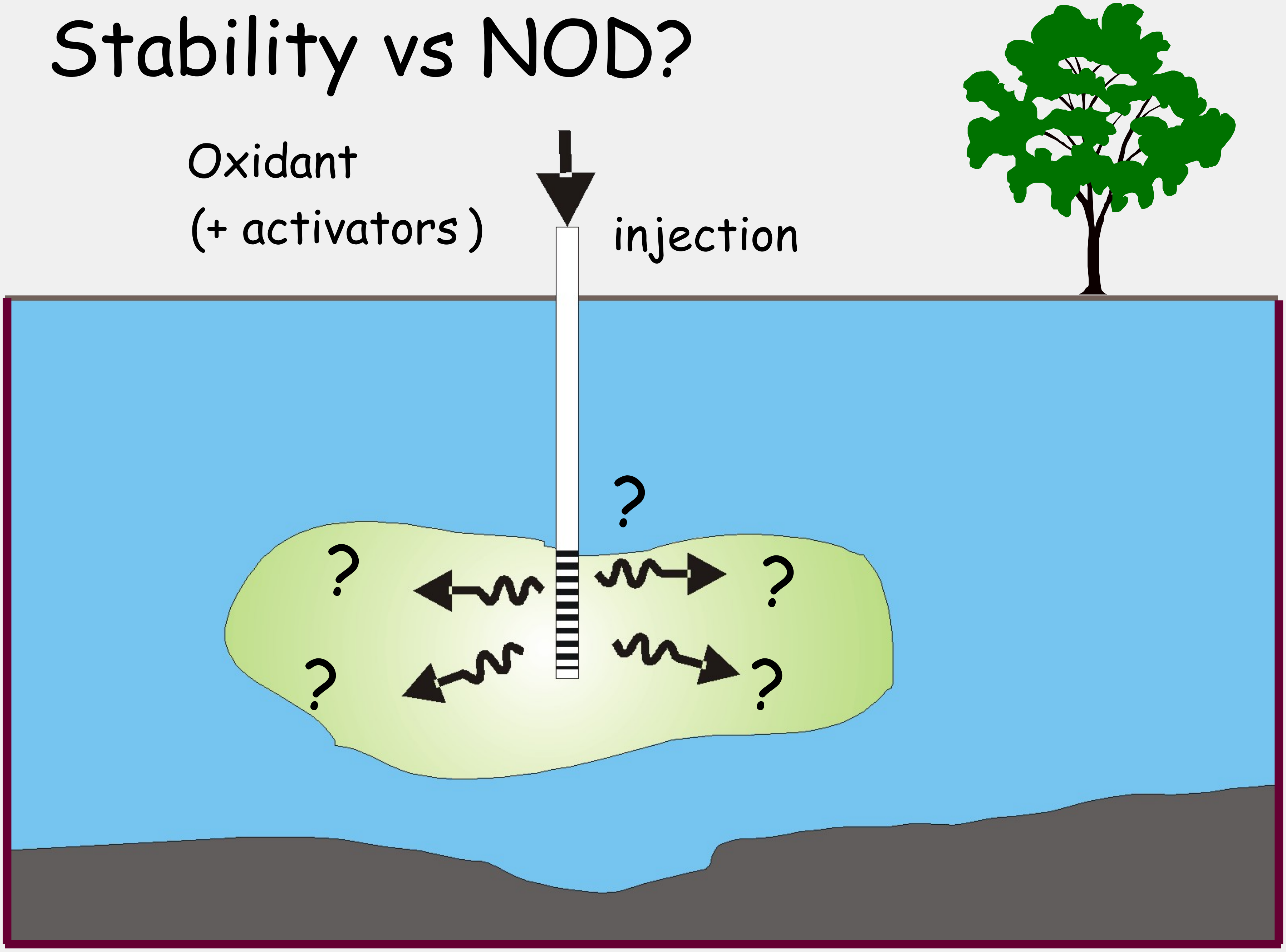
- consumption of oxidant
- decomposition rate

Decrease…

- transport/mobility
- the reaction rate
- mass of oxidant available

… inefficient treatment system

Stability vs NOD?



Approach

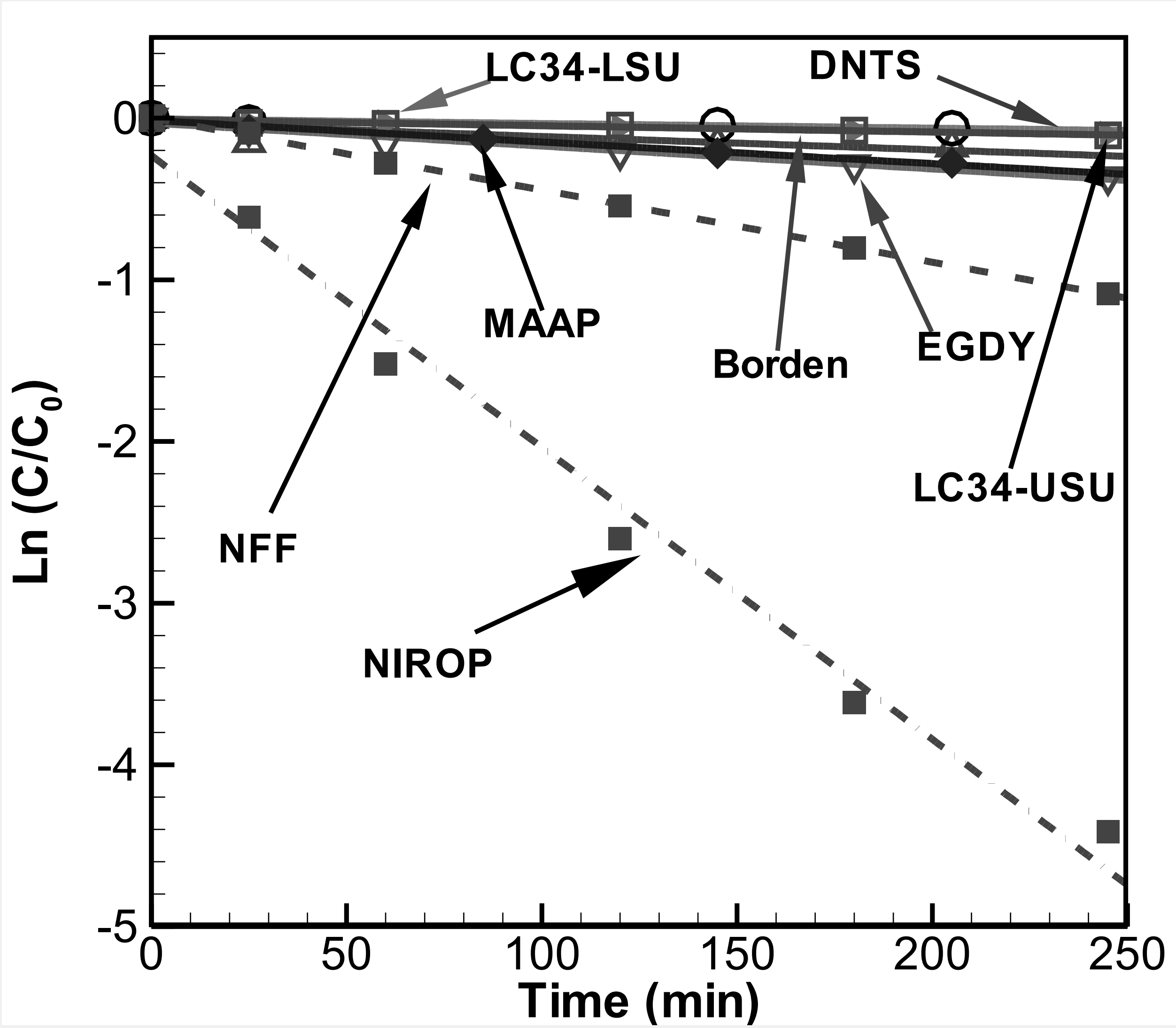
- Collect and characterize aquifer materials
- Perform a batch and column tests, and field experiments
- Develop kinetic models to capture observed trends
- Explore predictive implications

Site Locations

Peroxide Story…

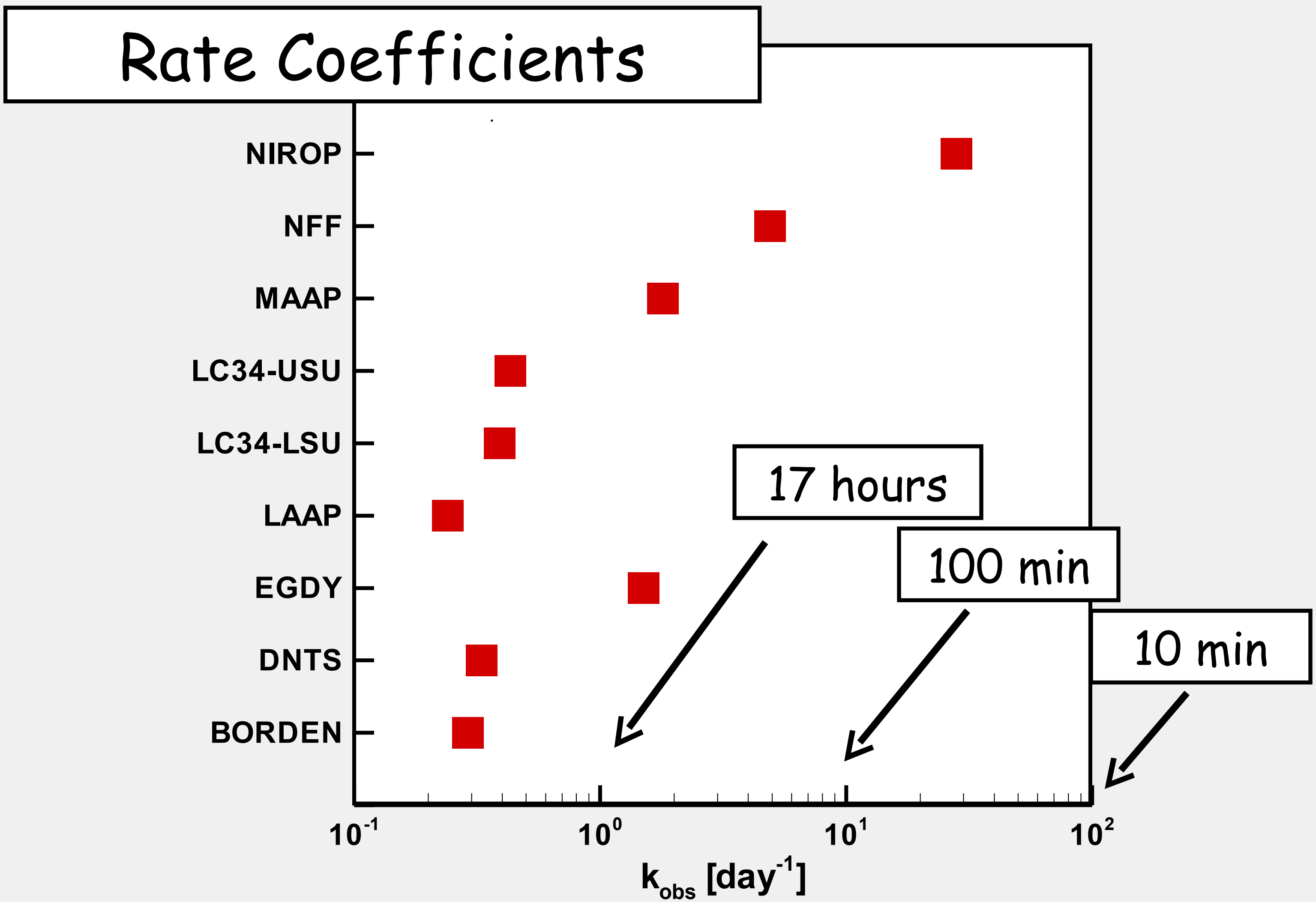
$$H_2O_2$$

Peroxide



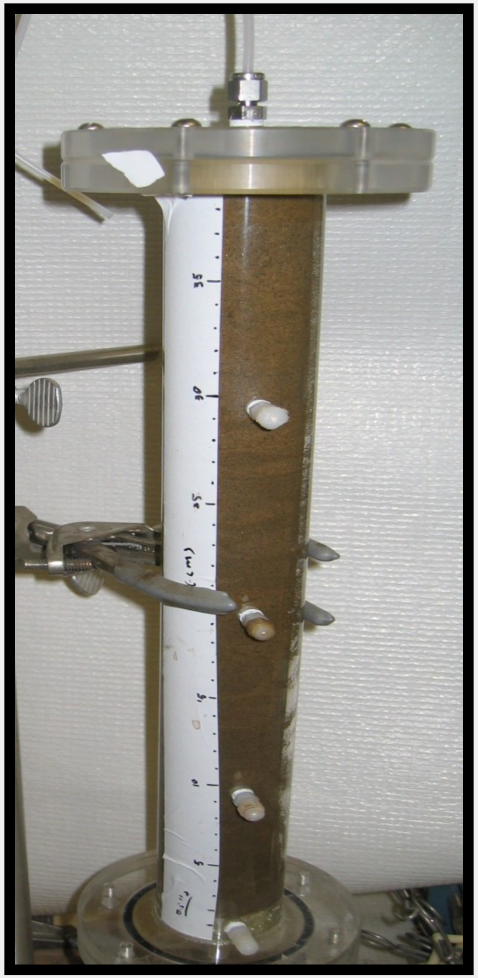
LC34-LSU
DNTS
MAAP
Borden
EGDY
LC34-USU
NFF
NIROP
Ln (C/C0)
Time (min)
0
-1
-2
-3
-4
-5
0
50
100
150
200
250

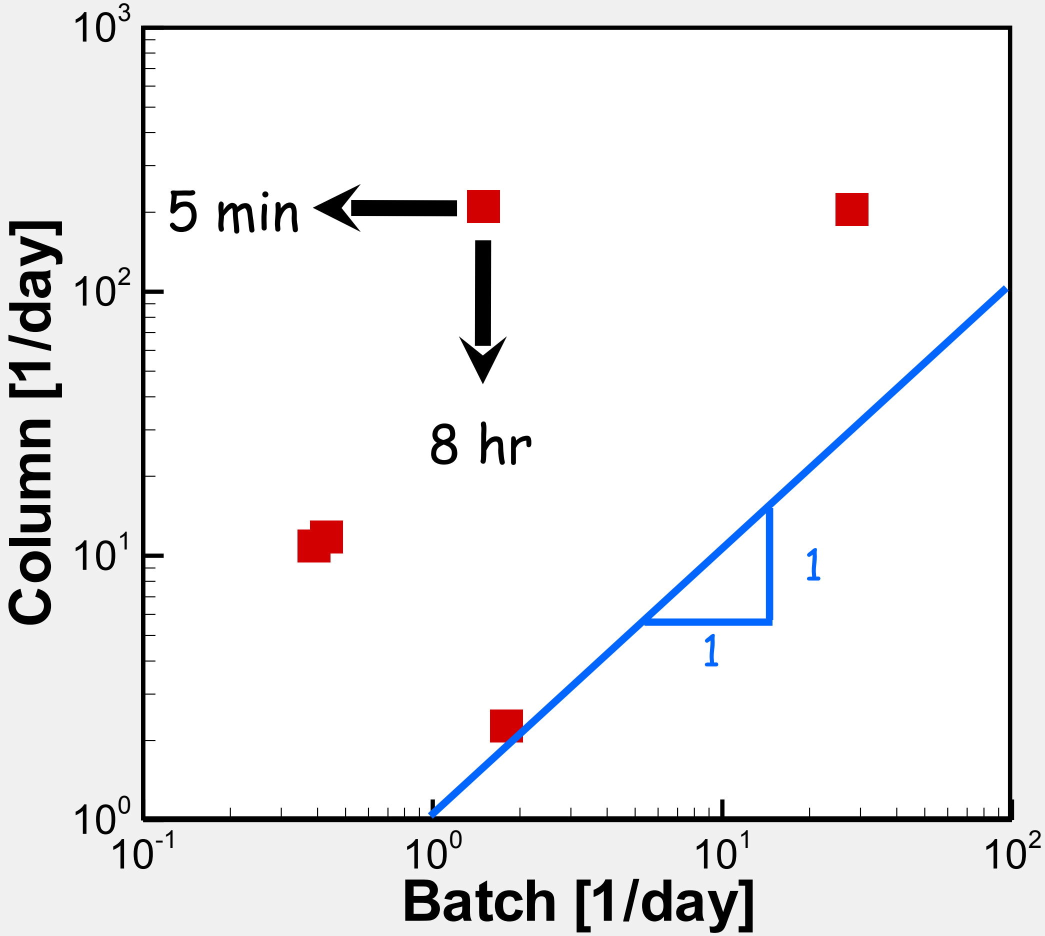
Peroxide

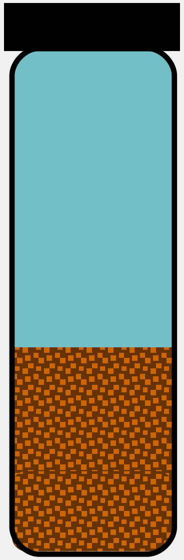

Rate Coefficients
NIROP
NFF
MAAP
LC34-USU
LC34-LSU
LAAP
EGDY
DNTS
BORDEN
17 hours
100 min
10 min
10^{-1}
10^{0}
10^{1}
10^{2}
k_{obs} [day^{-1}]

Peroxide

Rate Coefficients



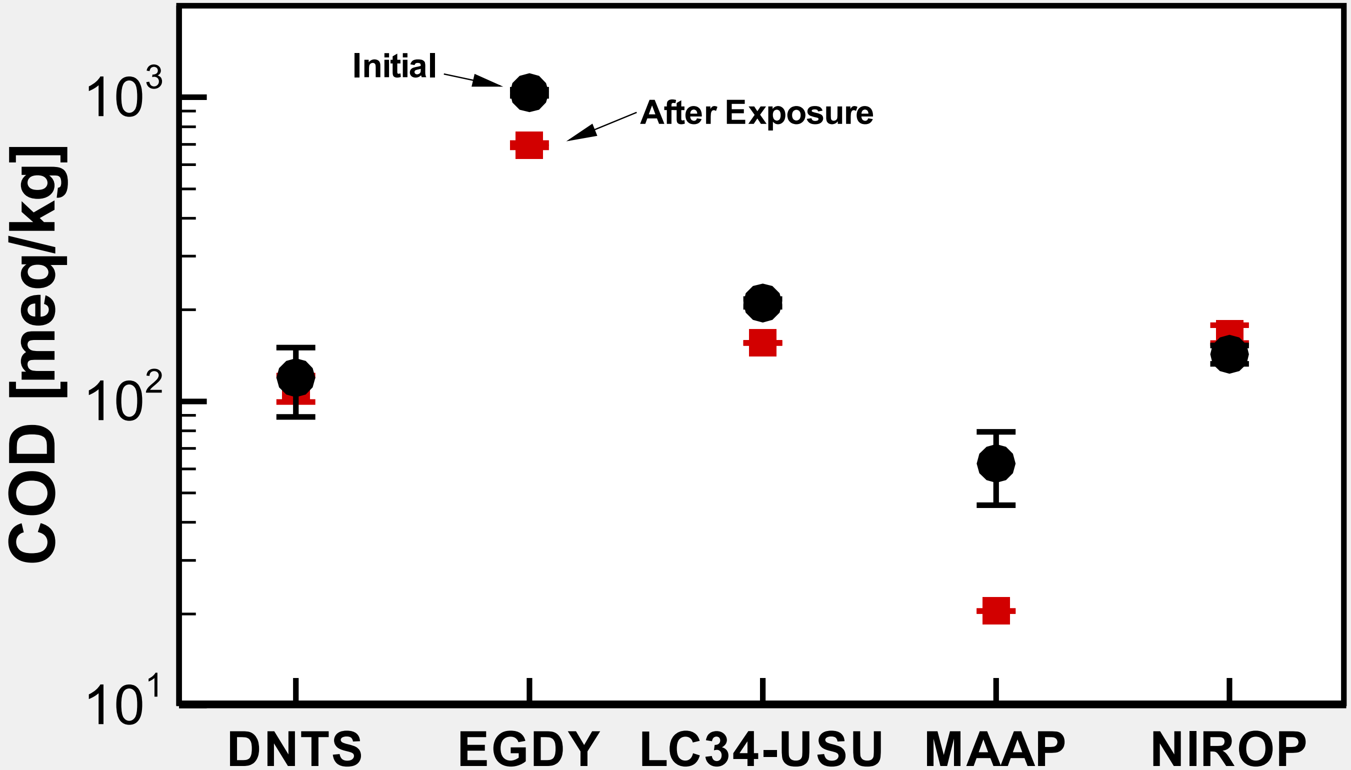




Peroxide

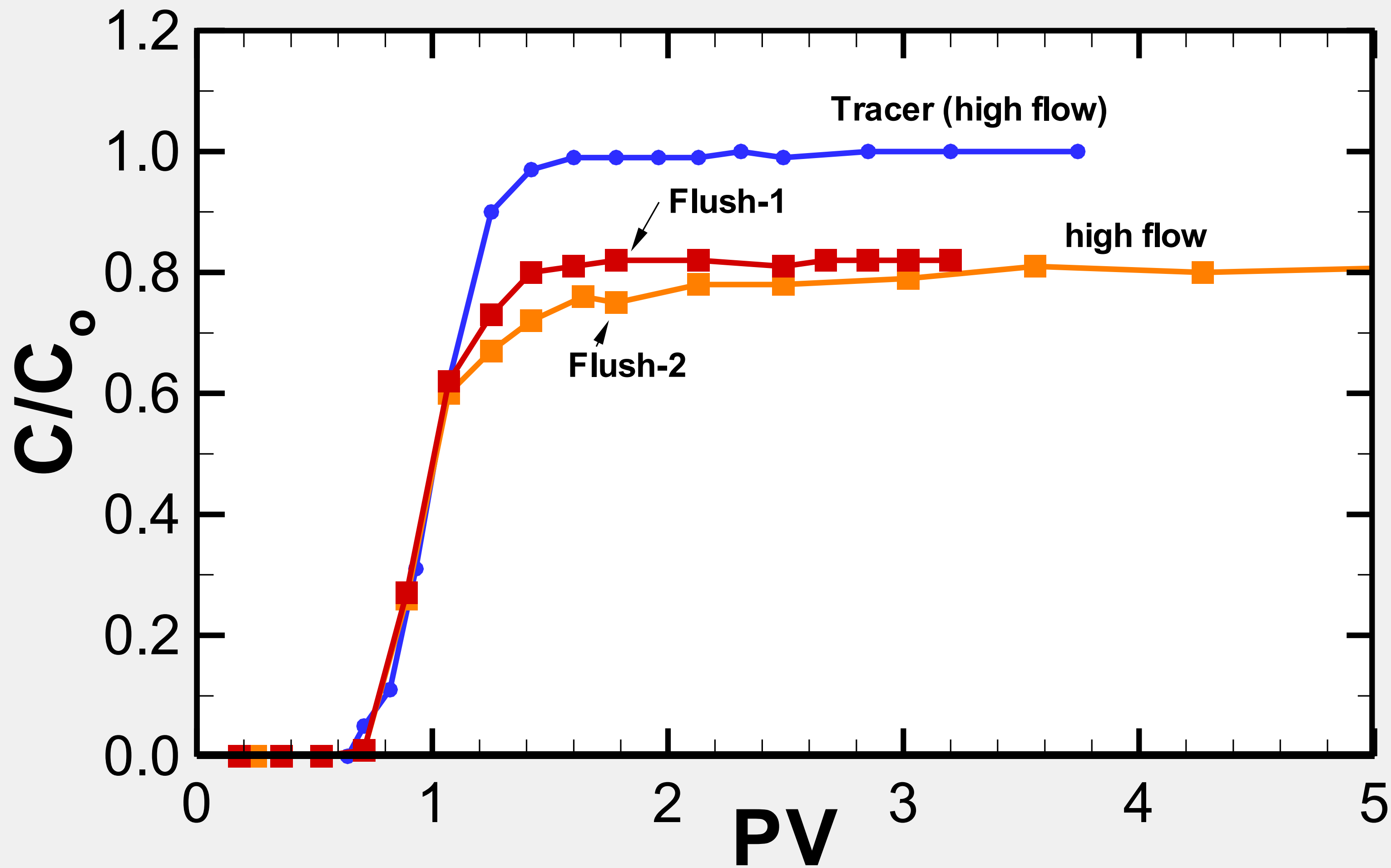
Change in TRC

TRC = total reductive capacity



Peroxide

Repeated Application



Peroxide Kinetics

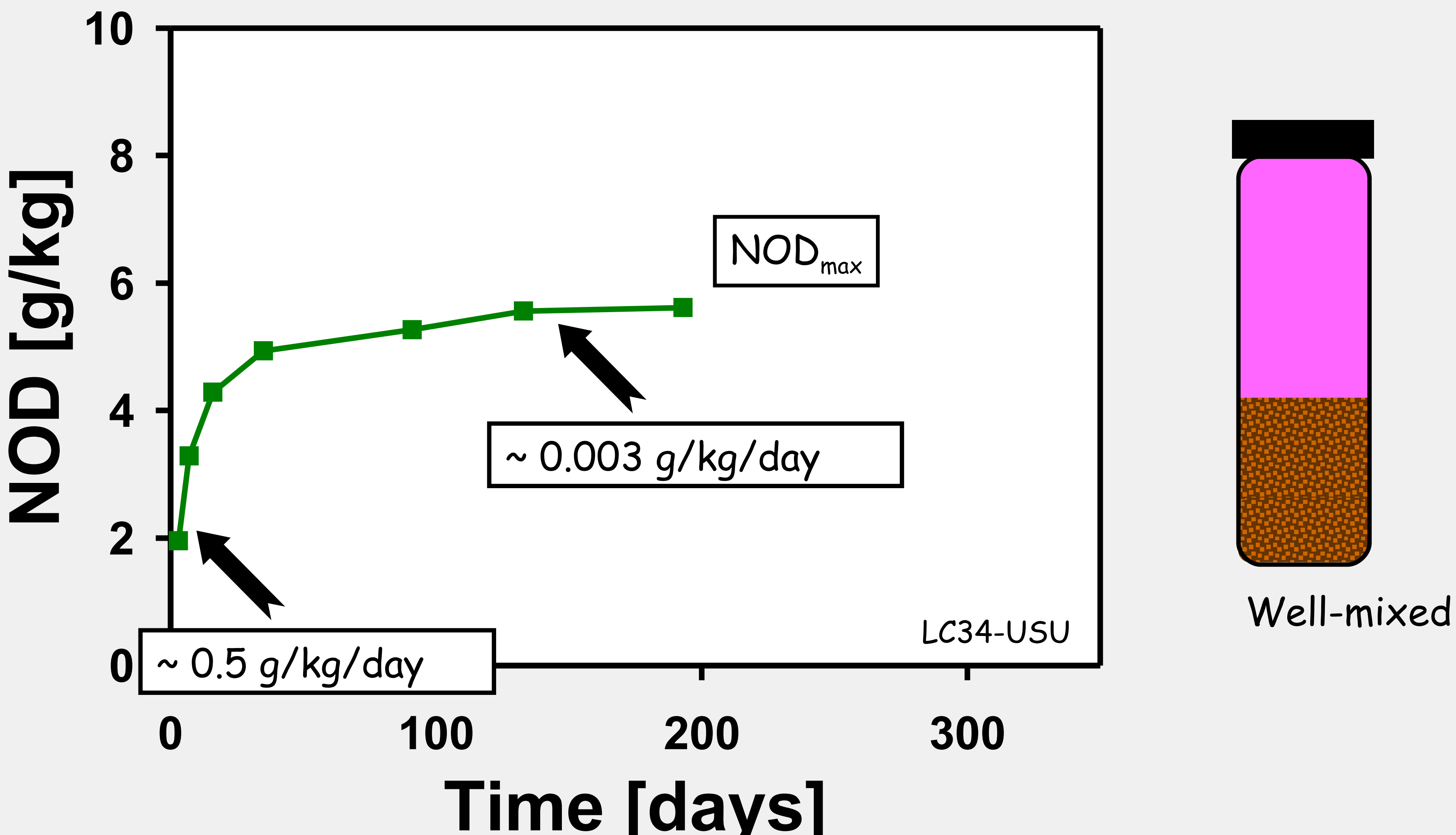
$$\frac{d(C_{H_2O_2})}{dt} = -k_{obs}\, C_{H_2O_2}$$

$$k_{obs} = 2.16[\text{amorphous Fe}] - 0.303 \quad (r^2 = 0.99)$$

Permanganate Story…

$$MnO_4^-$$

Typical Batch Reactor Results



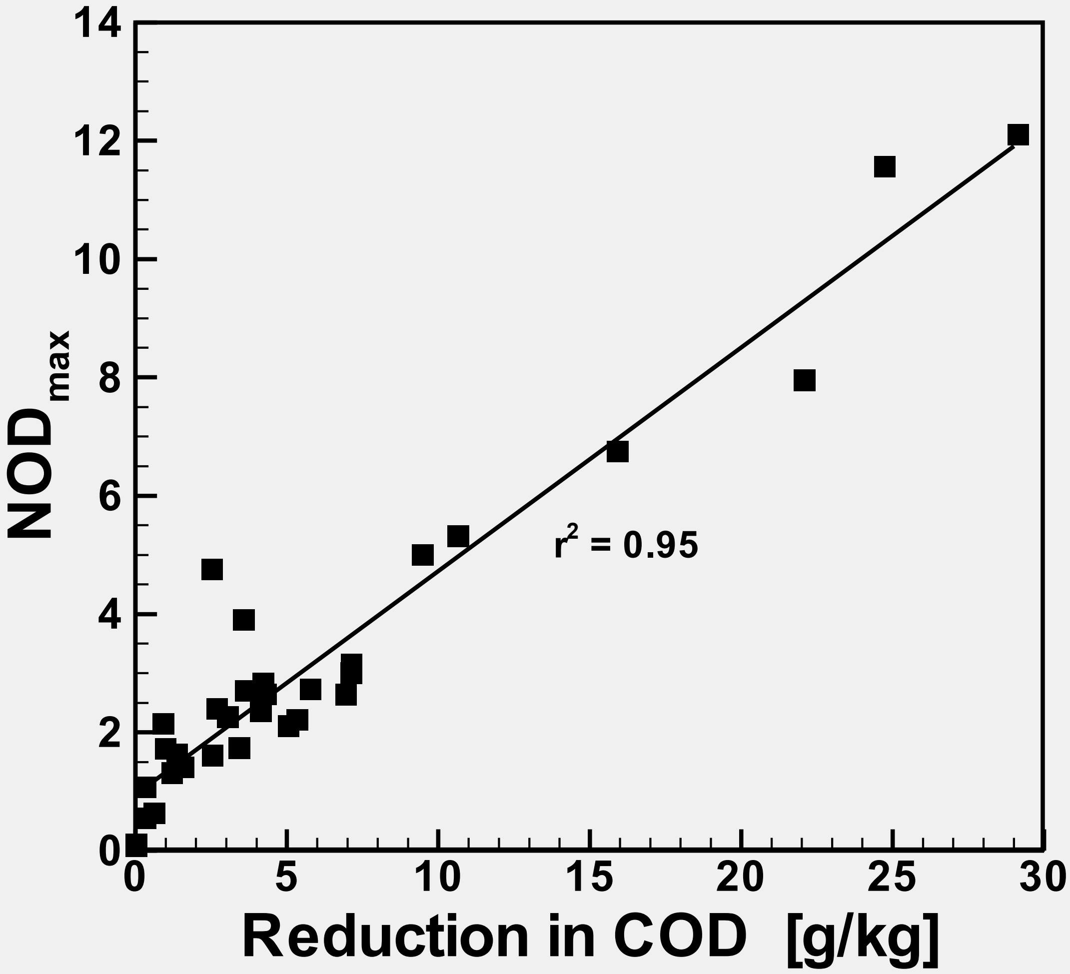
Permanganate
Natural Oxidant Demand (NOD)

Consumption by the naturally present reduced species associated with the aquifer material

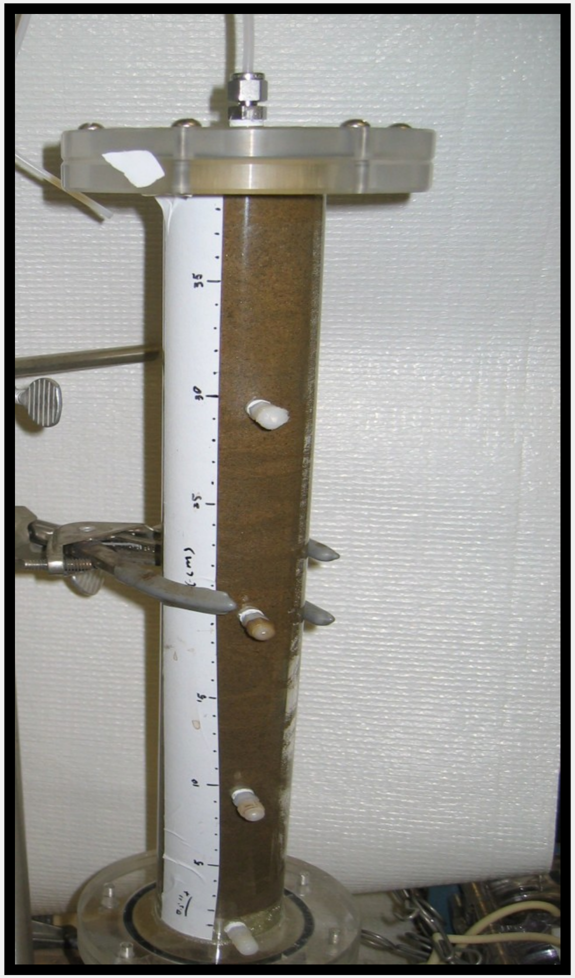
g of $KMnO_4$ / kg of solids

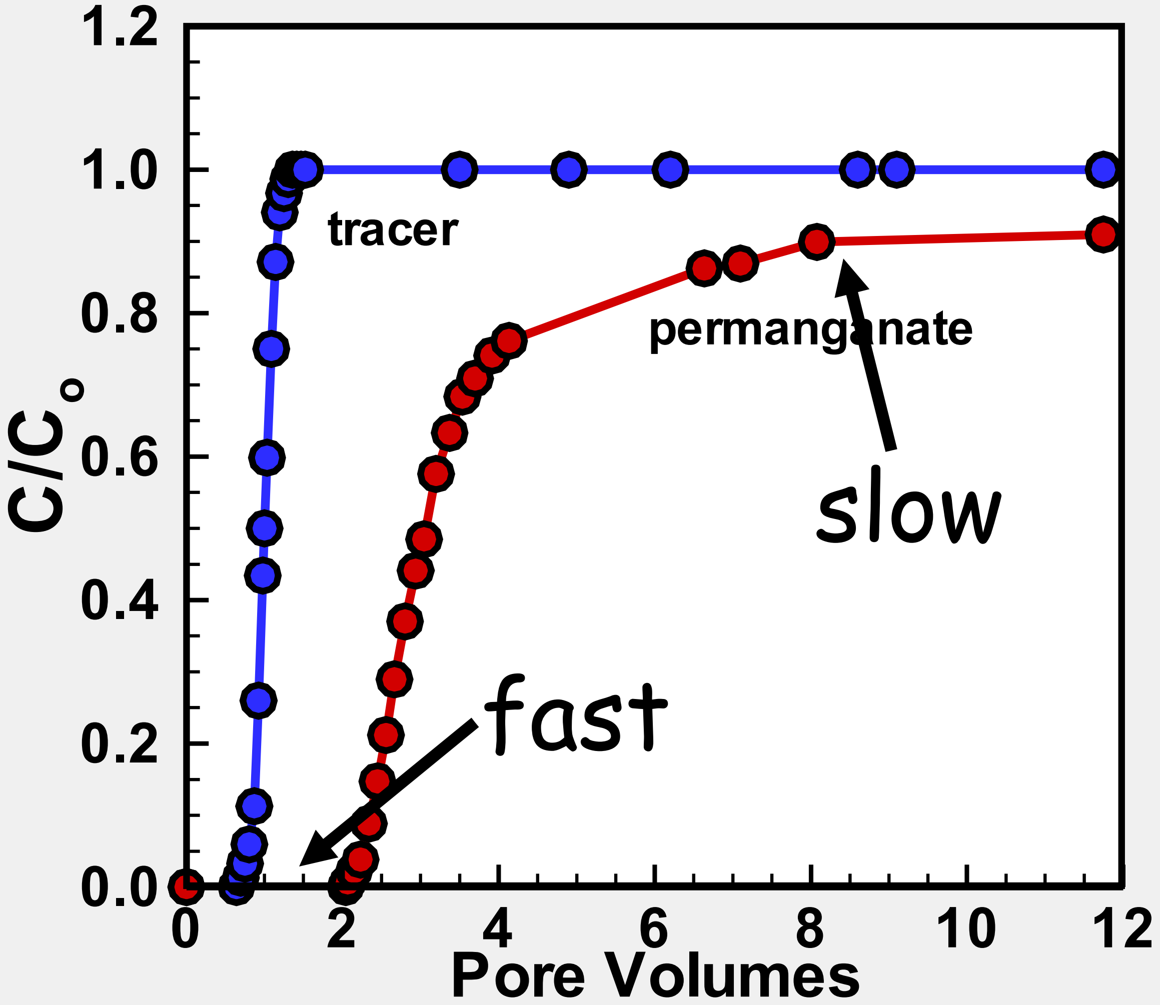
Permanganate

Change in TRC

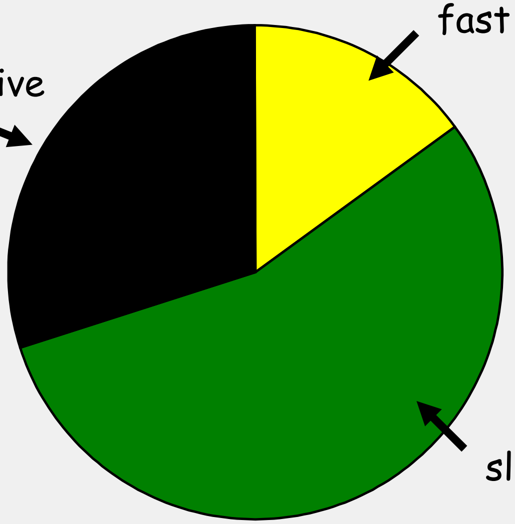


Column Experiments





Permanganate Kinetics



Fast

$$\frac{dC_{OAM}^{fast}}{dt} = -\, k_{OAM}^{fast}\, C_{OAM}^{\alpha\ fast}\, C_{MnO_4^-}^{\beta\ fast}$$

Slow

$$\frac{dC_{OAM}^{slow}}{dt} = -\, k_{OAM}^{slow}\, C_{OAM}^{\alpha\ slow}\, C_{MnO_4^-}^{\beta\ slow}$$

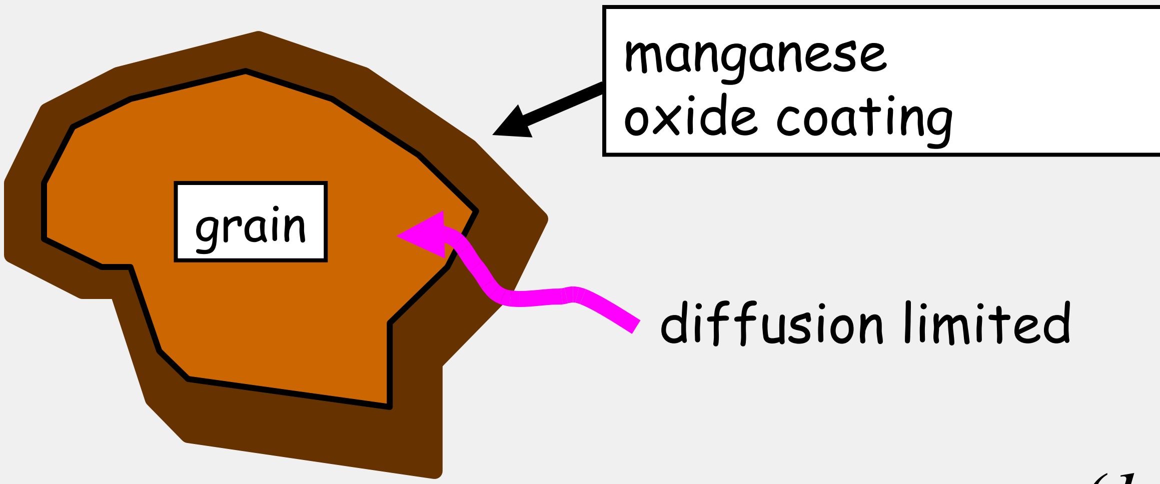
Permanganate

$$\frac{d\,C_{MnO_4^-}}{dt} = -\, k_{MnO_4^-}^{fast}\, C_{OAM}^{\alpha\ fast}\, C_{MnO_4^-}^{\beta\ fast} -\, k_{MnO_4^-}^{slow}\, C_{OAM}^{\alpha\ slow}\, C_{MnO_4^-}^{\beta\ slow}$$

Passivation?

Hypothesis

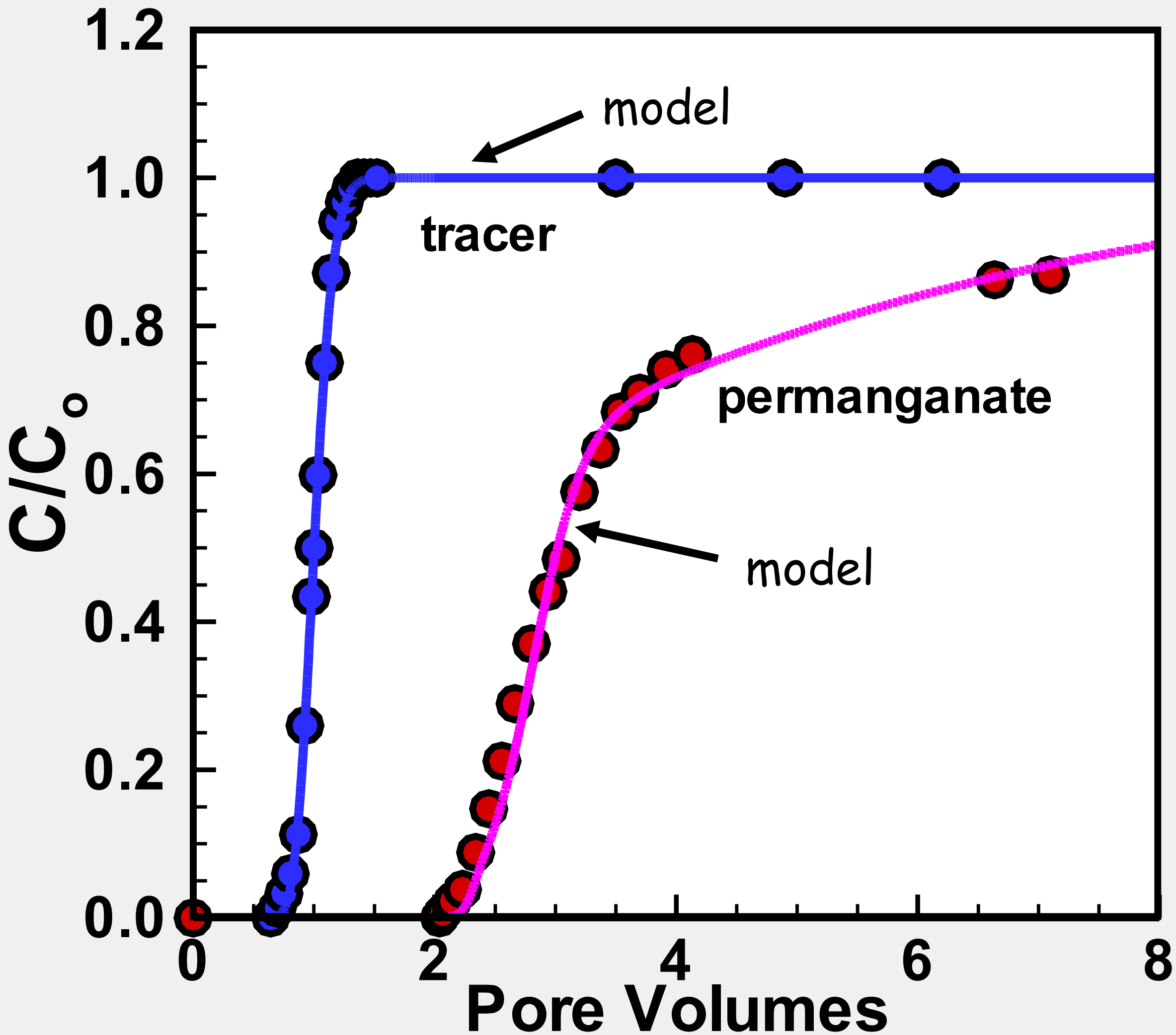
- reaction rate decreases as manganese oxides form

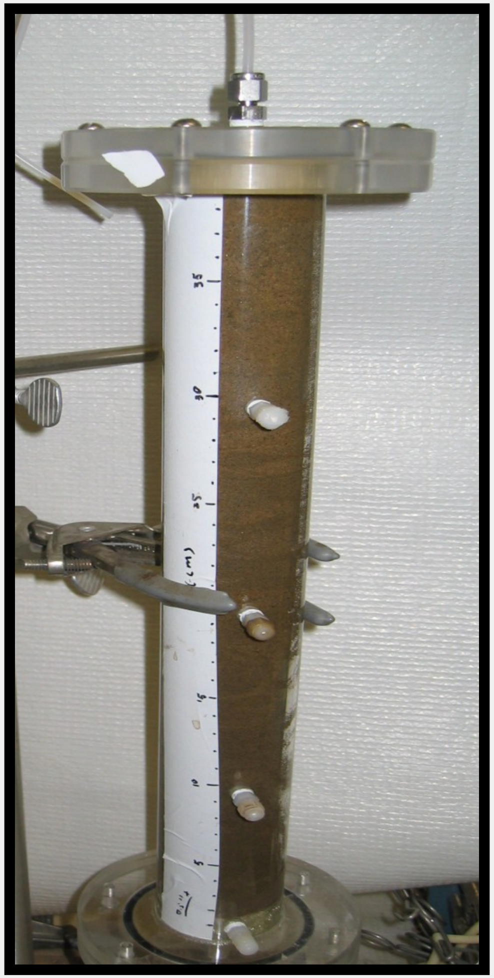


$$k_{OAM}^{slow}(MnO_2) = \frac{(k_{OAM}^{slow})_{initial}}{1 + \kappa\ C_{MnO_2}}$$

Passivation?

Column Data - Model Results

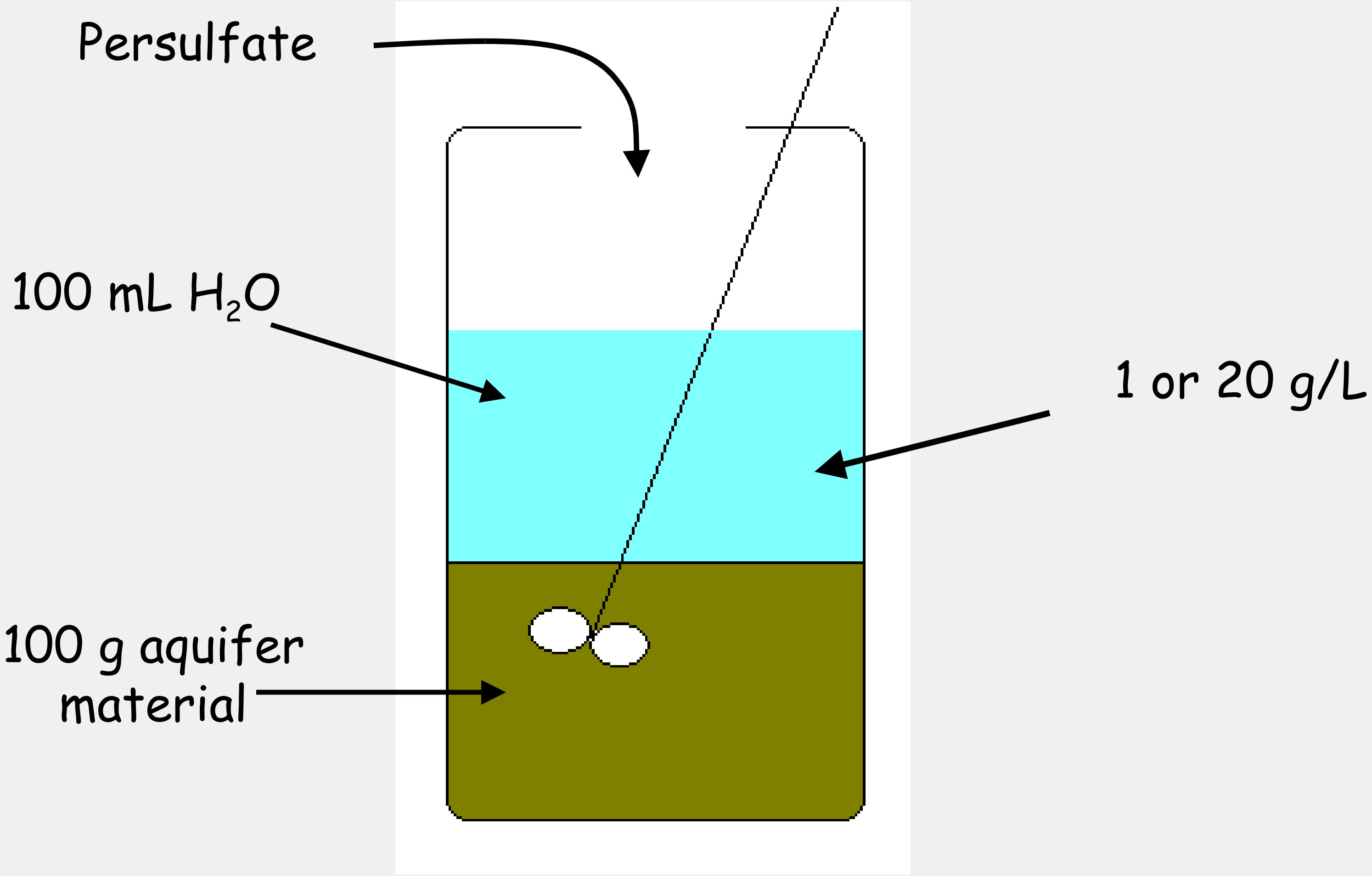




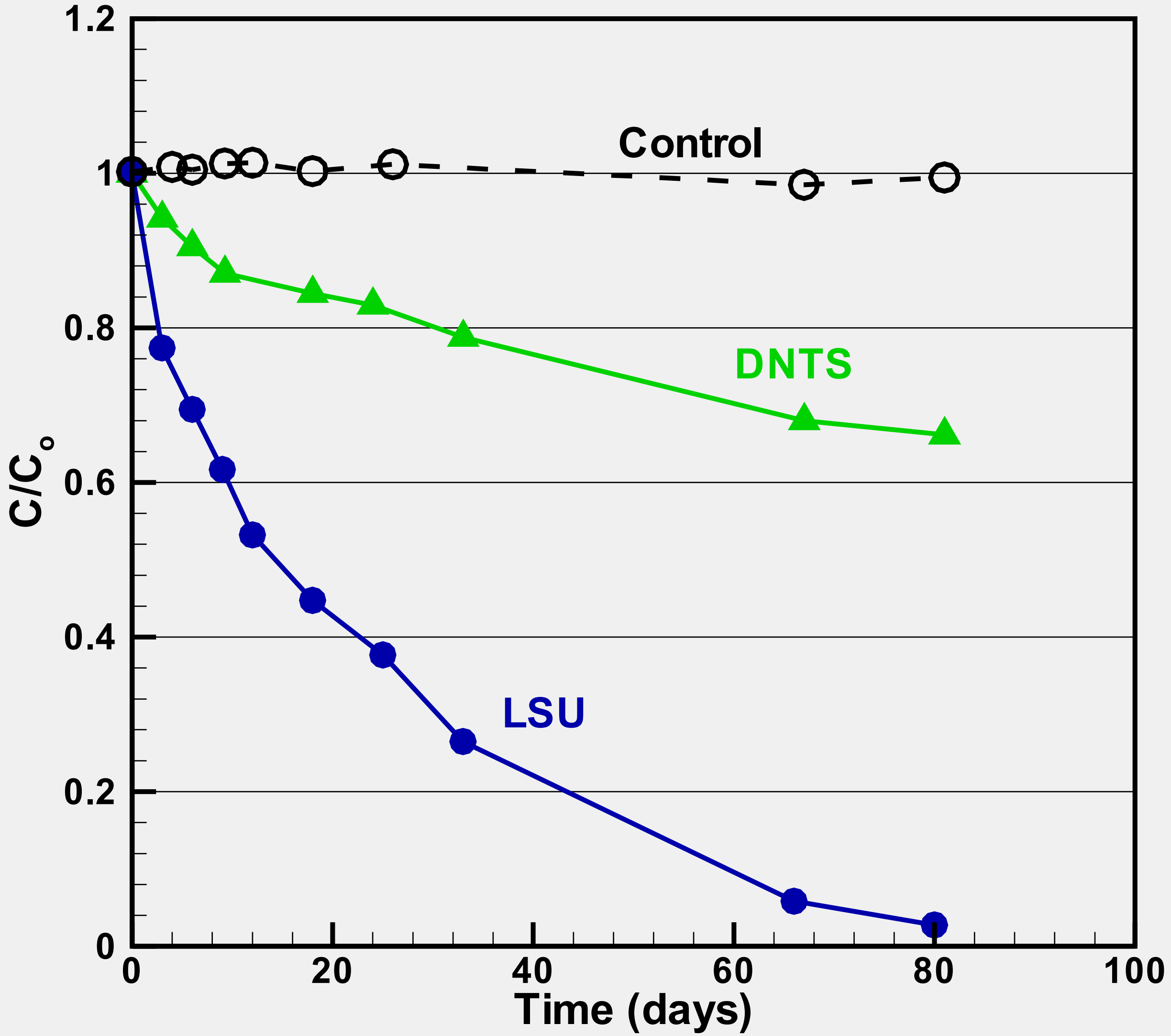
Persulfate Story…

$$S_2O_4^{2-}$$

Persulfate

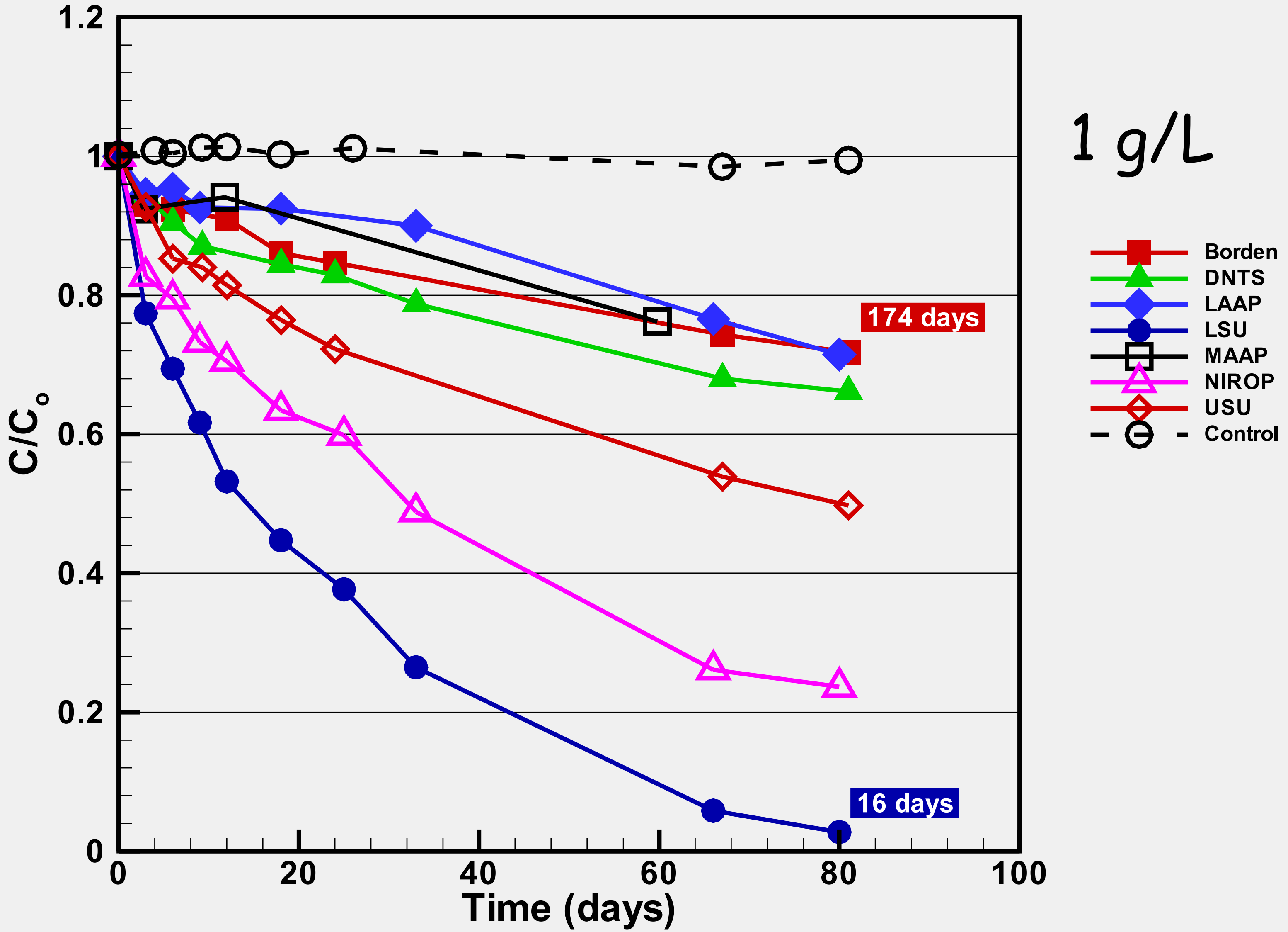


Persulfate



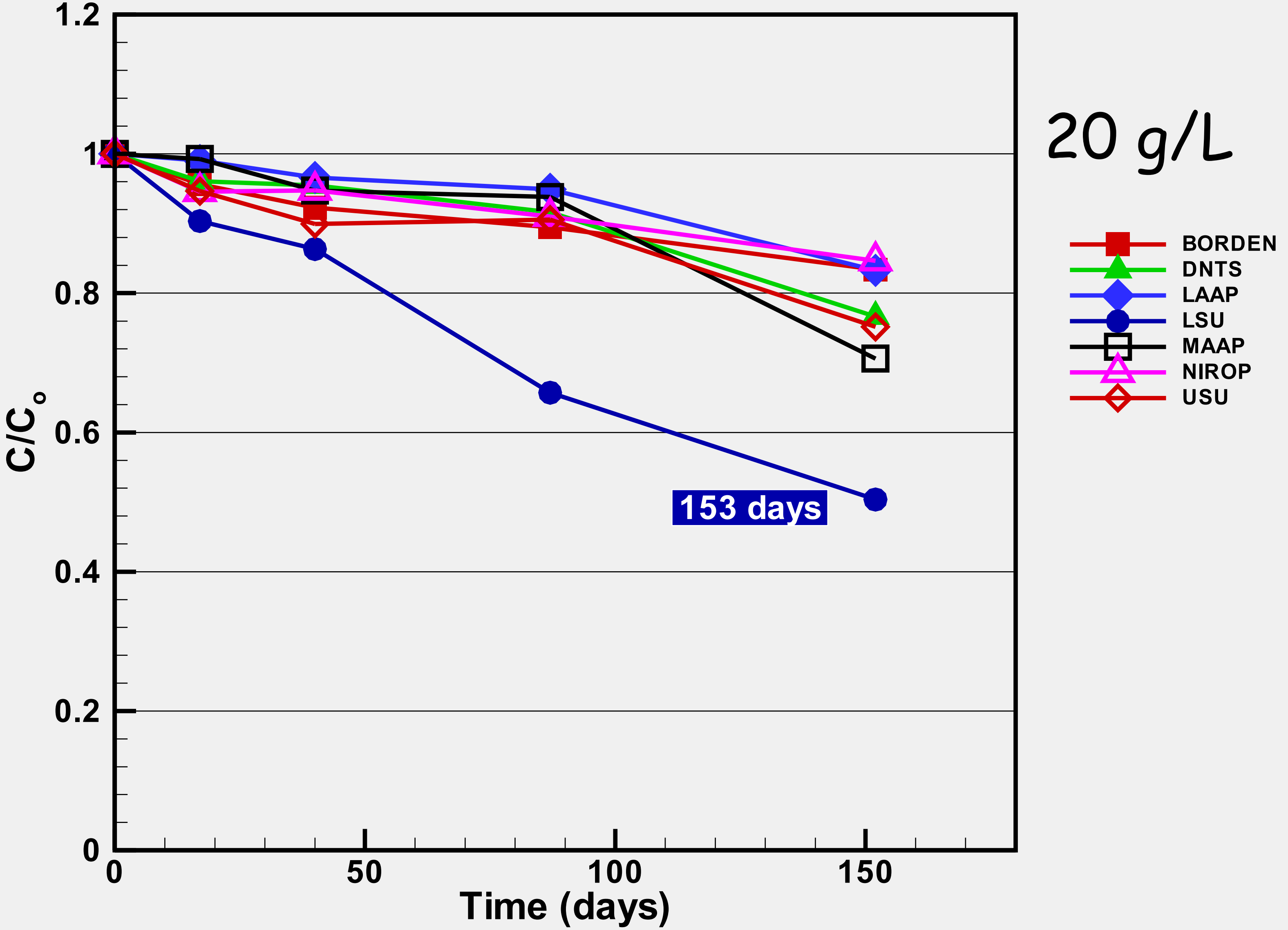
1 g/L

Persulfate



1 g/L
C/Co
Time (days)
174 days
16 days
Borden
DNTS
LAAP
LSU
MAAP
NIROP
USU
Control

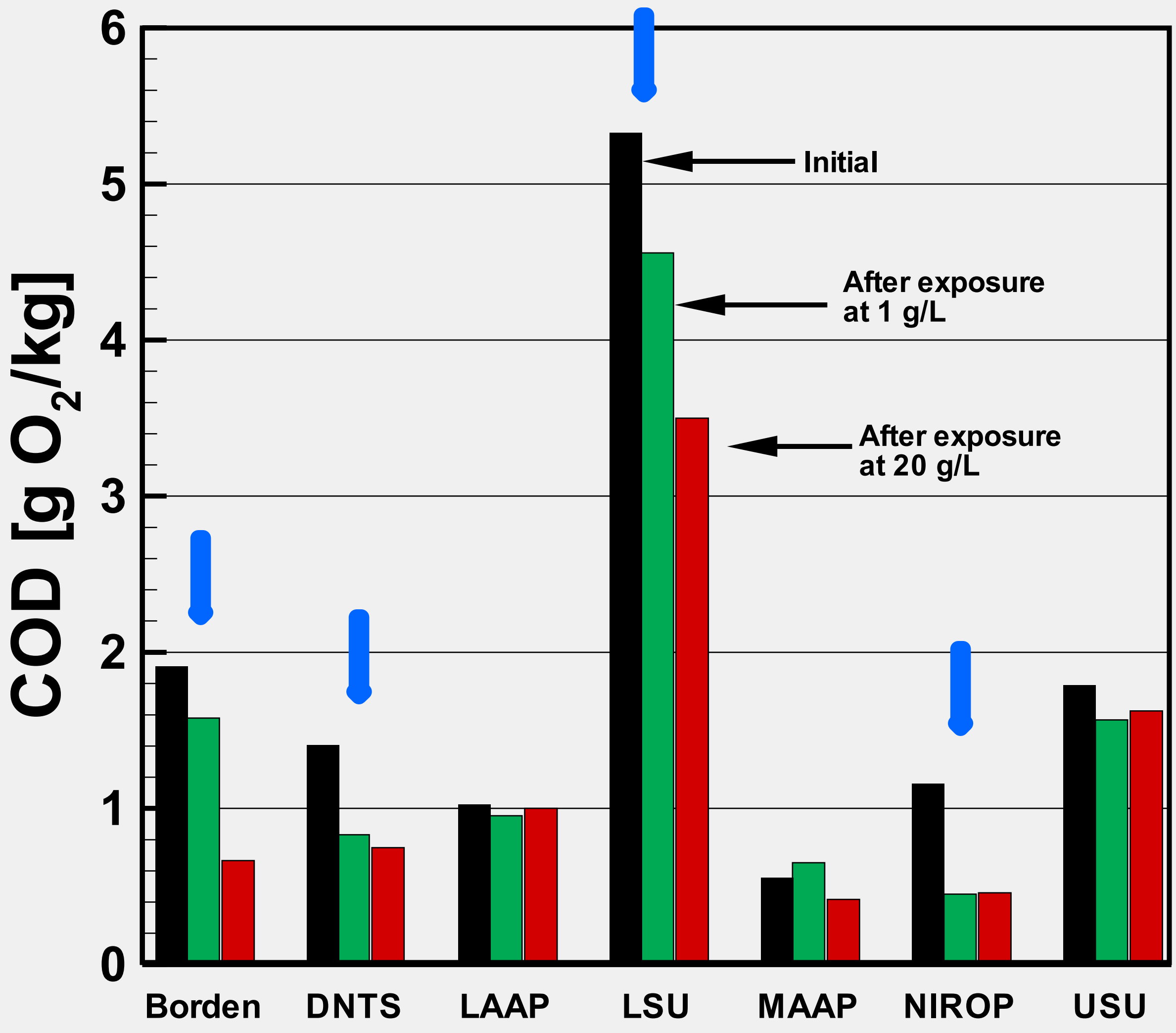
Persulfate



1.2
1
0.8
0.6
0.4
0.2
0
C/Co
0
50
100
150
Time (days)
153 days
20 g/L
BORDEN
DNTS
LAAP
LSU
MAAP
NIROP
USU

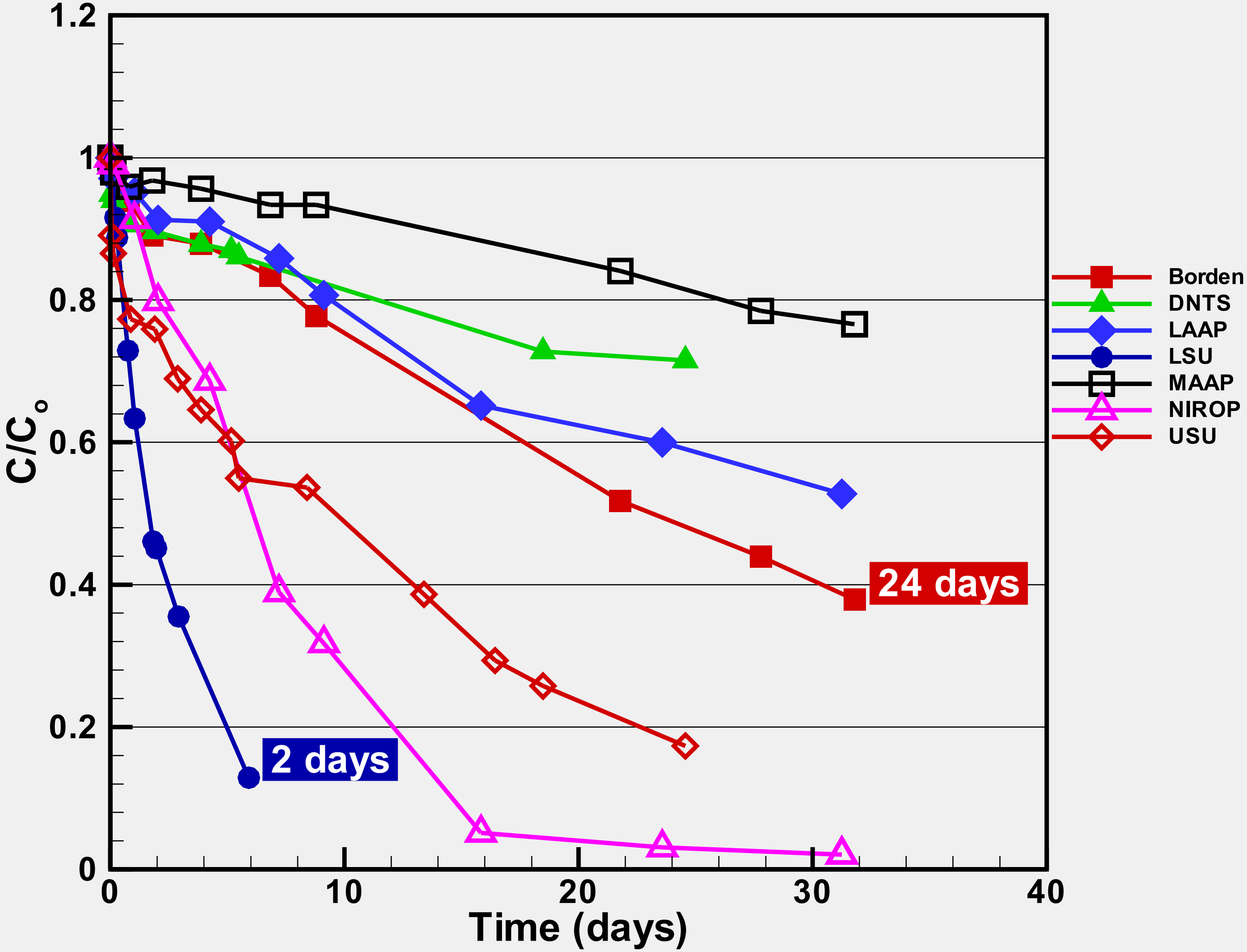
Persulfate

Change in TRC

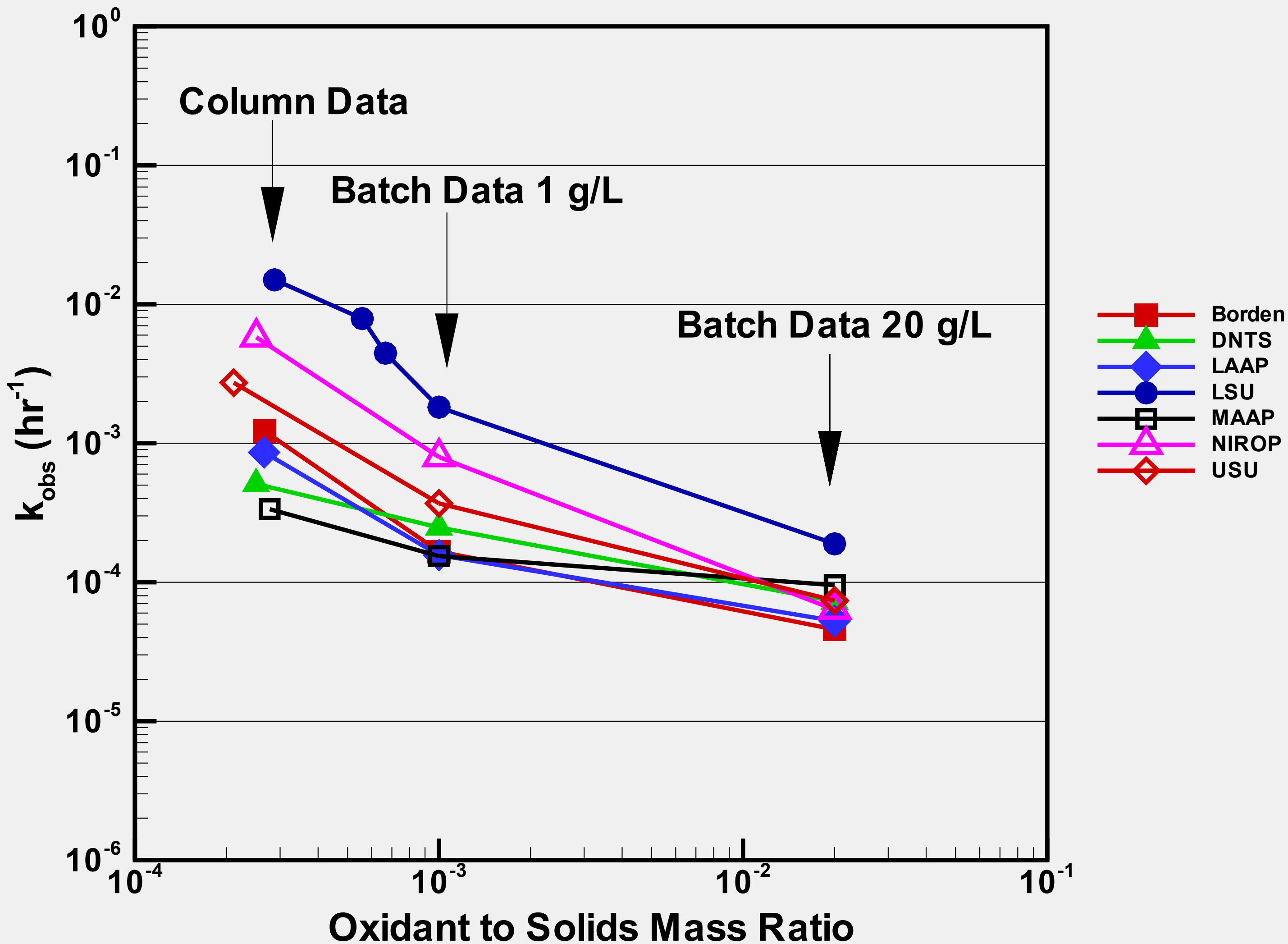


Persulfate

Stop-flow column



Persulfate



Column Data
Batch Data 1 g/L
Batch Data 20 g/L
k_{obs} (hr^{-1})
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Oxidant to Solids Mass Ratio
Borden
DNTS
LAAP
LSU
MAAP
NIROP
USU

Persulfate Kinetics

$$\frac{d[S_2O_8^{2-}]}{dt} = -k_1[S_2O_8^{2-}] - k_2[H^+][S_2O_8^{2-}] = -(k_1 + k_2[H^+])[S_2O_8^{2-}]$$

uncatalyzed degradation

acid catalyzed degradation

$$\frac{d[S_2O_8^{2-}]}{dt} = -(k_1 + k_2[H^+])[S_2O_8^{2-}]$$

$$- k_{cat}[S_2O_8^{2-}][C_{cat}]^{n_{cat}} - k_{NOM}[S_2O_8^{2-}][C_{NOM}]^{n_{NOM}}$$

mineral catalyzed reaction

NOM reaction

Persulfate

$$\frac{d[S_2O_8^{2-}]}{dt} = -k_{bulk}[S_2O_8^{2-}]$$

$$k_{bulk} = \gamma_{S_2O_8^{2-}} \left(\begin{array}{l} k_1 \\ + \gamma_{H^+} \; k_2[H^+] \\ + \gamma_{cat}^{1.5} \, k_{cat}[C_{cat}]^{1.5} \\ + \gamma_{NOM}^{1.5} \; k_{NOM}[C_{NOM}]^{1.5} \end{array} \right)$$

← uncatalyzed

← acid catalyzed

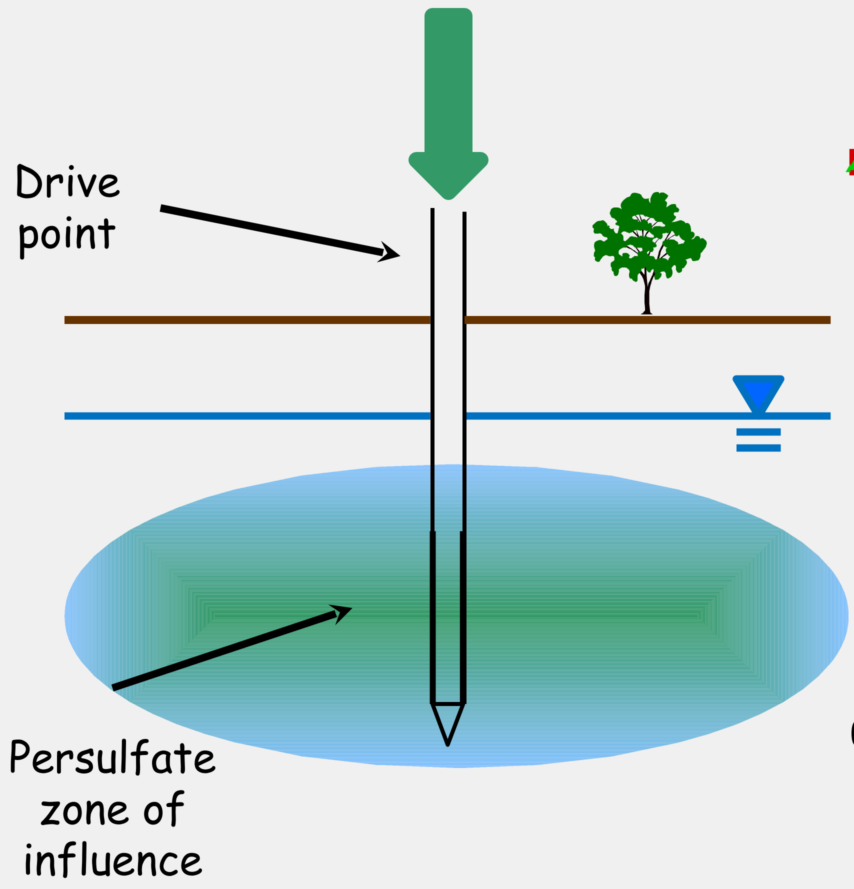
← mineral reaction

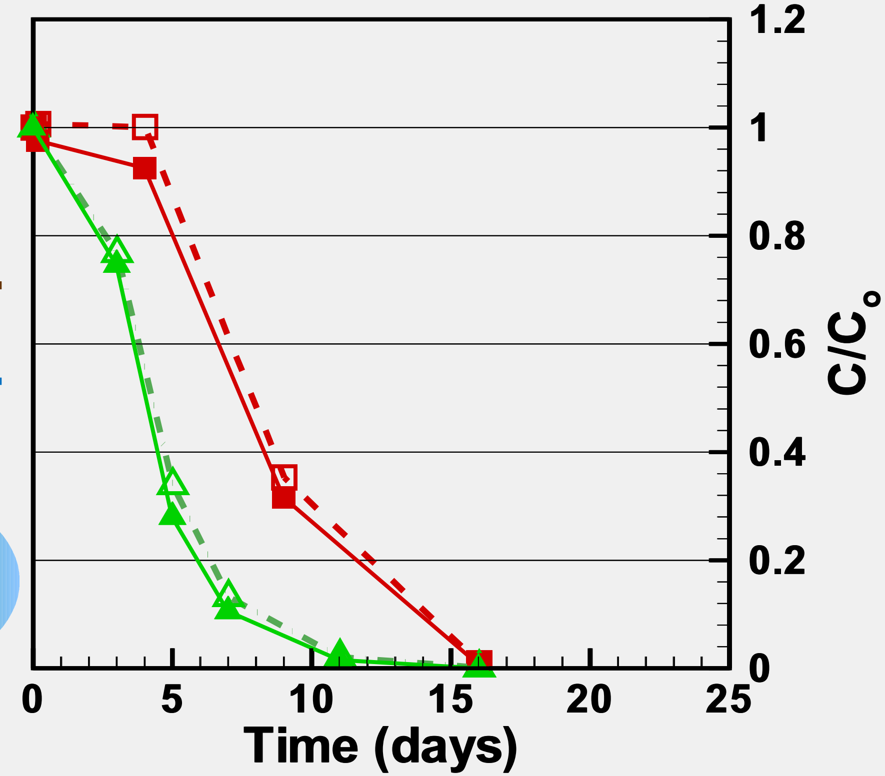
← NOM reaction

↑ activity coefficients

Persulfate

Push-Pull test





Oxidant Stability vs NOD

Enhanced Decomposition

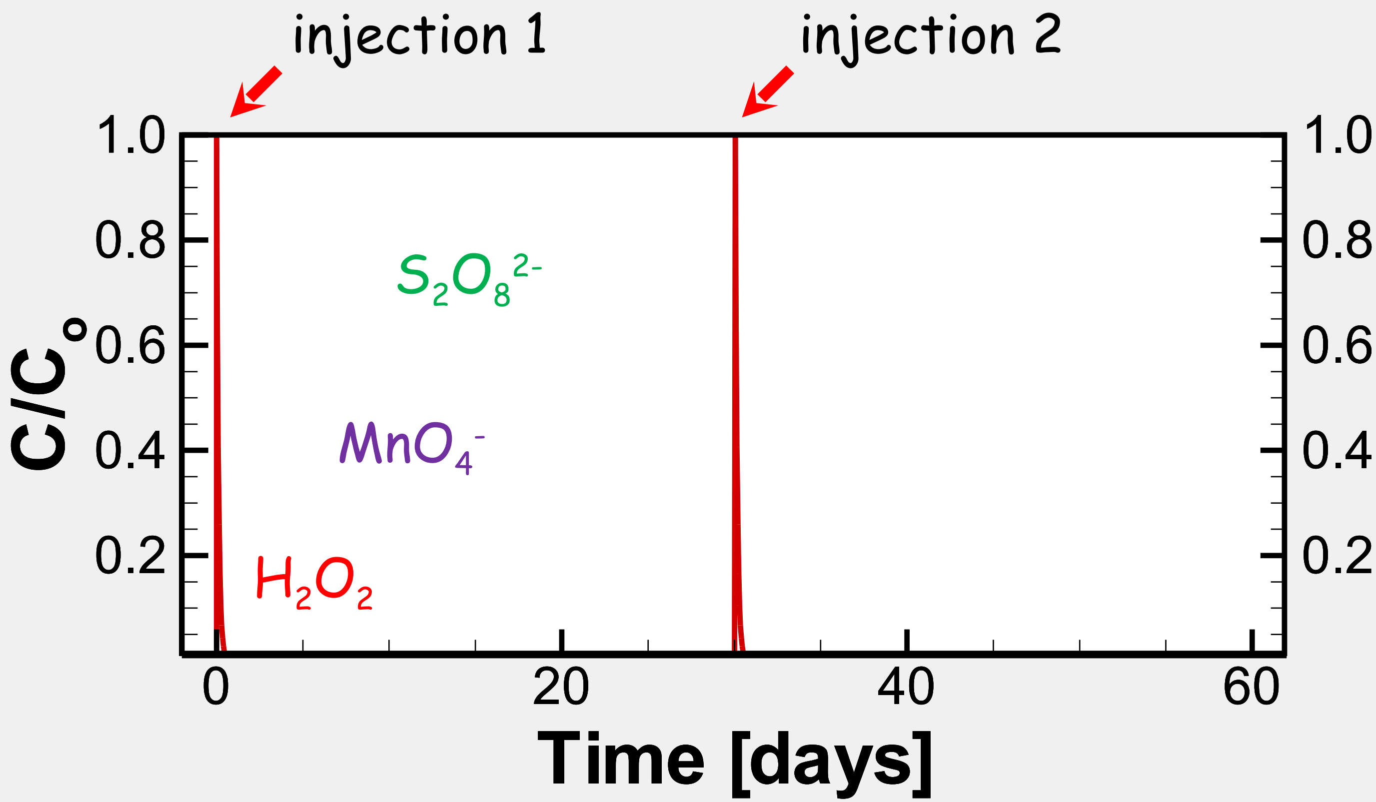
- H_2O_2 (little reduction in TRC)
- $S_2O_8^{2-}$ (slight/moderate reduction in TRC)

Finite Demand (NOD)

- MnO_4^- (proportional reduction in TRC)

Comparison - In Situ Injection

no flow or diffusion / same oxidation strength



Summary

- Ignoring aquifer material interaction will overestimate treatment efficiency
- Kinetic models developed for in situ conditions, but rely on properties...
  - H_2O_2 (amorphous Fe)
  - MnO_4^- (NOM)
  - $S_2O_8^{2-}$ (amorphous Fe + NOM)
- Bench-scale data are hindered by experimental conditions and scale-up issues

Questions?

University of Waterloo

Comparison

Site	H_2O_2	MnO_4^-	$S_2O_8^{2-}$
Borden	low	low	mid
DNTS	low	low	low
EGDY	mid	high	-
LC34-LSU	low	mid	highest
LC34-USU	low	mid	high
MAAP	mid	low	low
NFF	high	highest	-
NIROP	highest	low	high