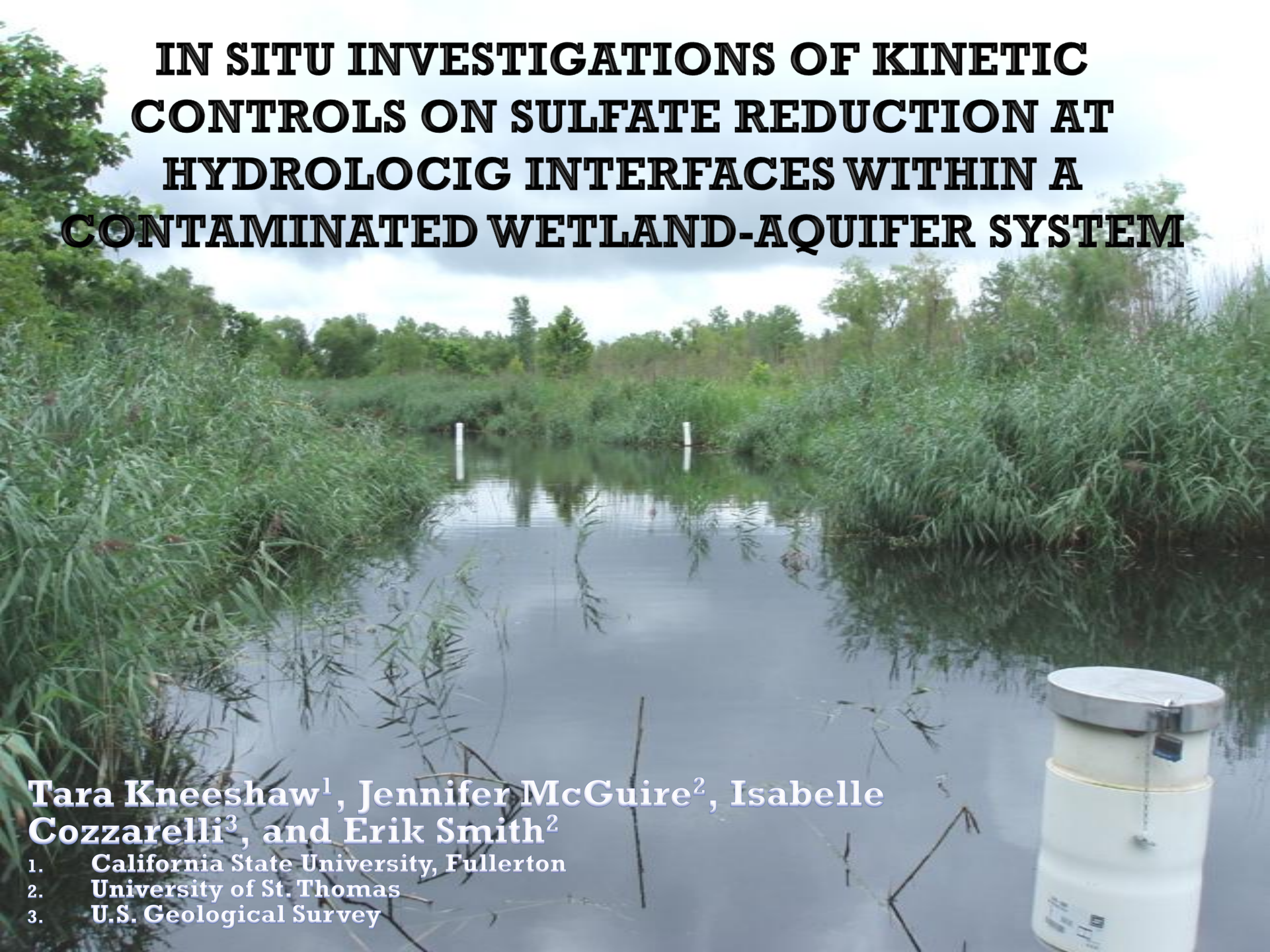

IN SITU INVESTIGATIONS OF KINETIC CONTROLS ON SULFATE REDUCTION AT HYDROLOCIG INTERFACES WITHIN A CONTAMINATED WETLAND-AQUIFER SYSTEM

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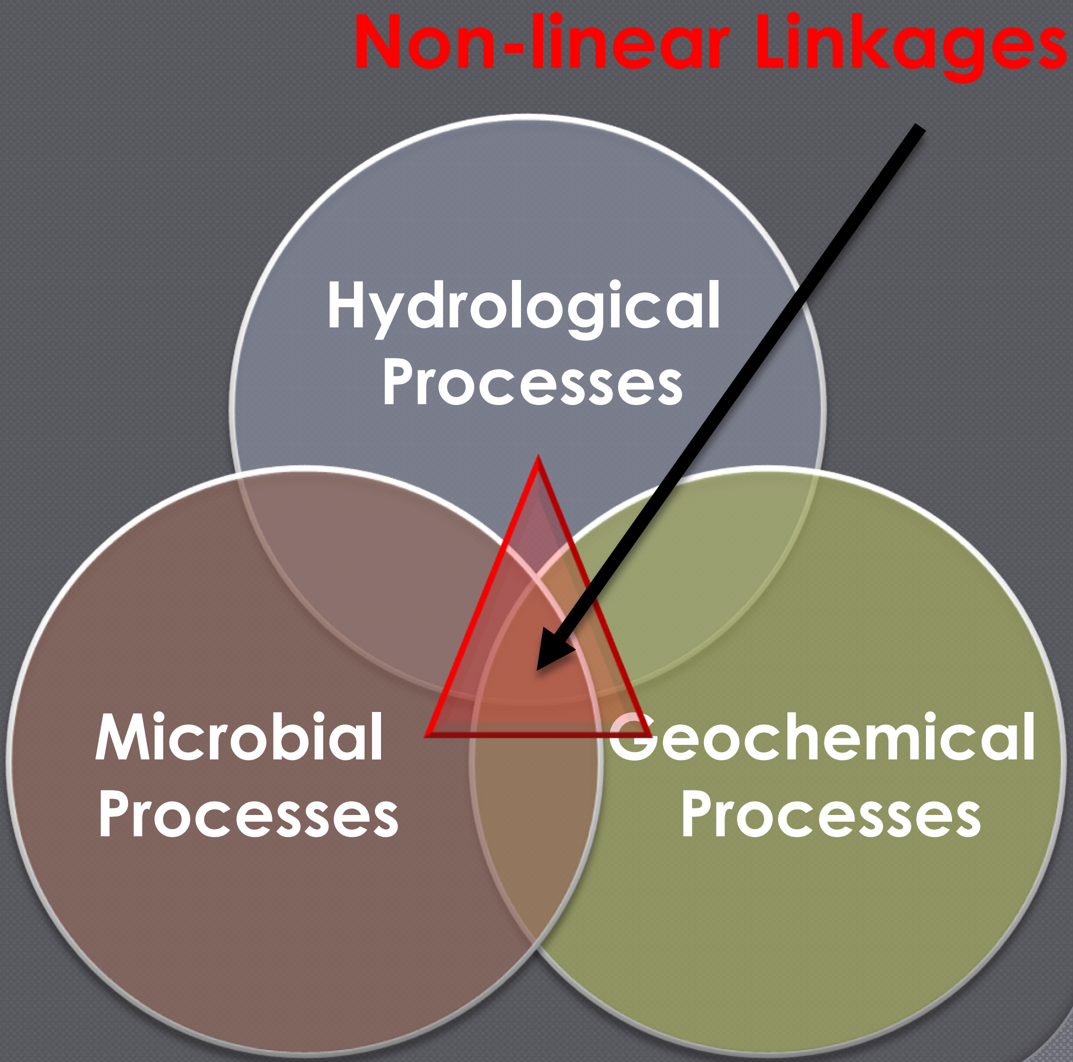
3. U.S. Geological Survey

Challenges

What do we need to know to study chemical fate and transport?

Cycles are linked



Systems as a whole must be studied to understand linkages

Role of Mixing Interfaces

Mixing Interfaces: Are they "hot spots" of biogeochemical cycling?

Mixing Interface

Can we quantify the role of mixing interfaces in biogeochemical cycling of natural systems?

Fundamental Issue

Water resource protection

- To predict chemical form, mobility, and toxicity, we need to ***quantify rates*** of reactions in dynamic environments.

Sulfate and Iron Reduction

Fundamental Issue

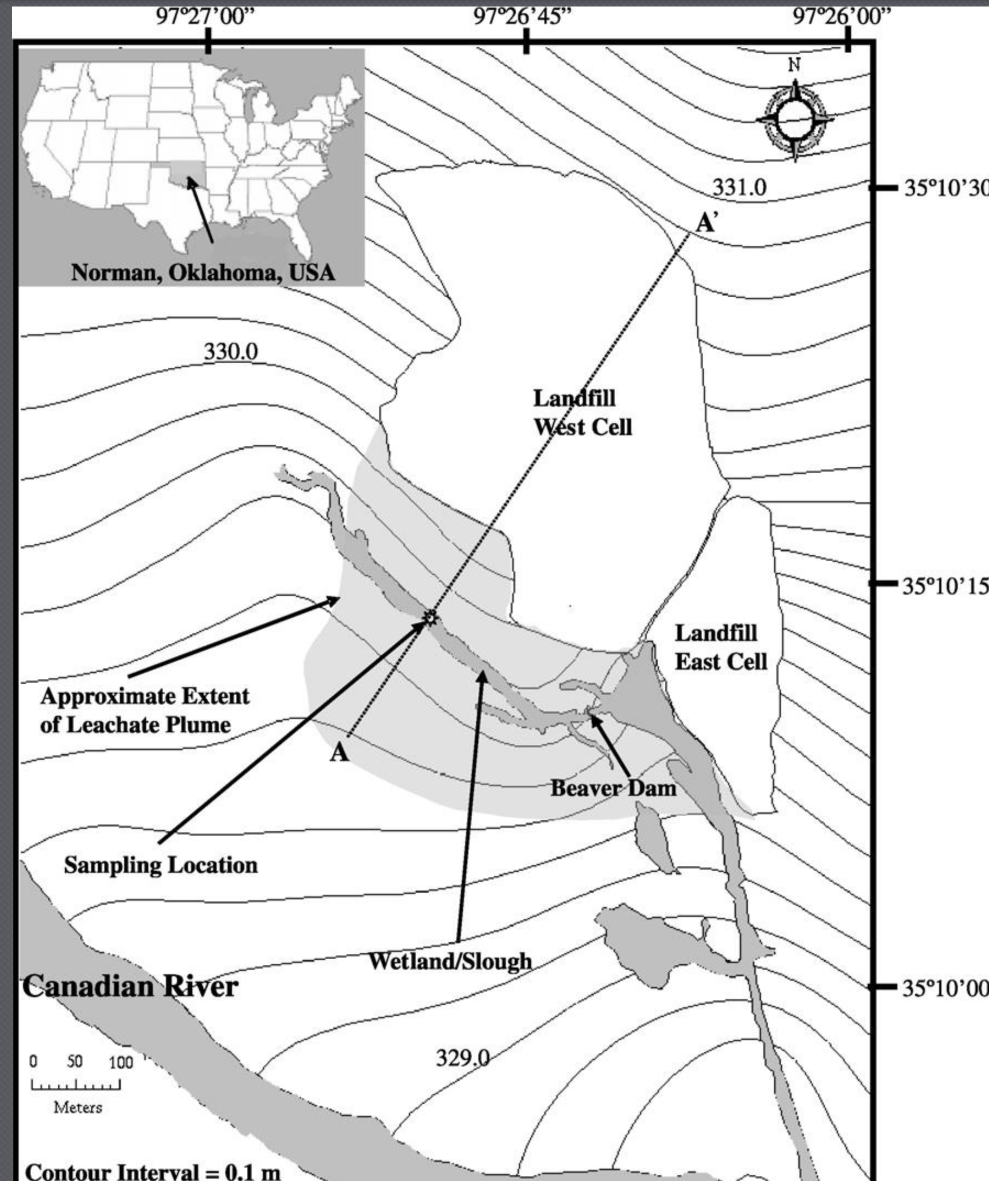
- rate estimates range many orders of magnitude (5)!
- Natural Systems are dynamic and often not at equilibrium.

Sulfate and Iron Reduction

ISSUE: Determine key kinetic controls on reactions…..

Study Site

Norman Landfill Research Site, Norman, OK



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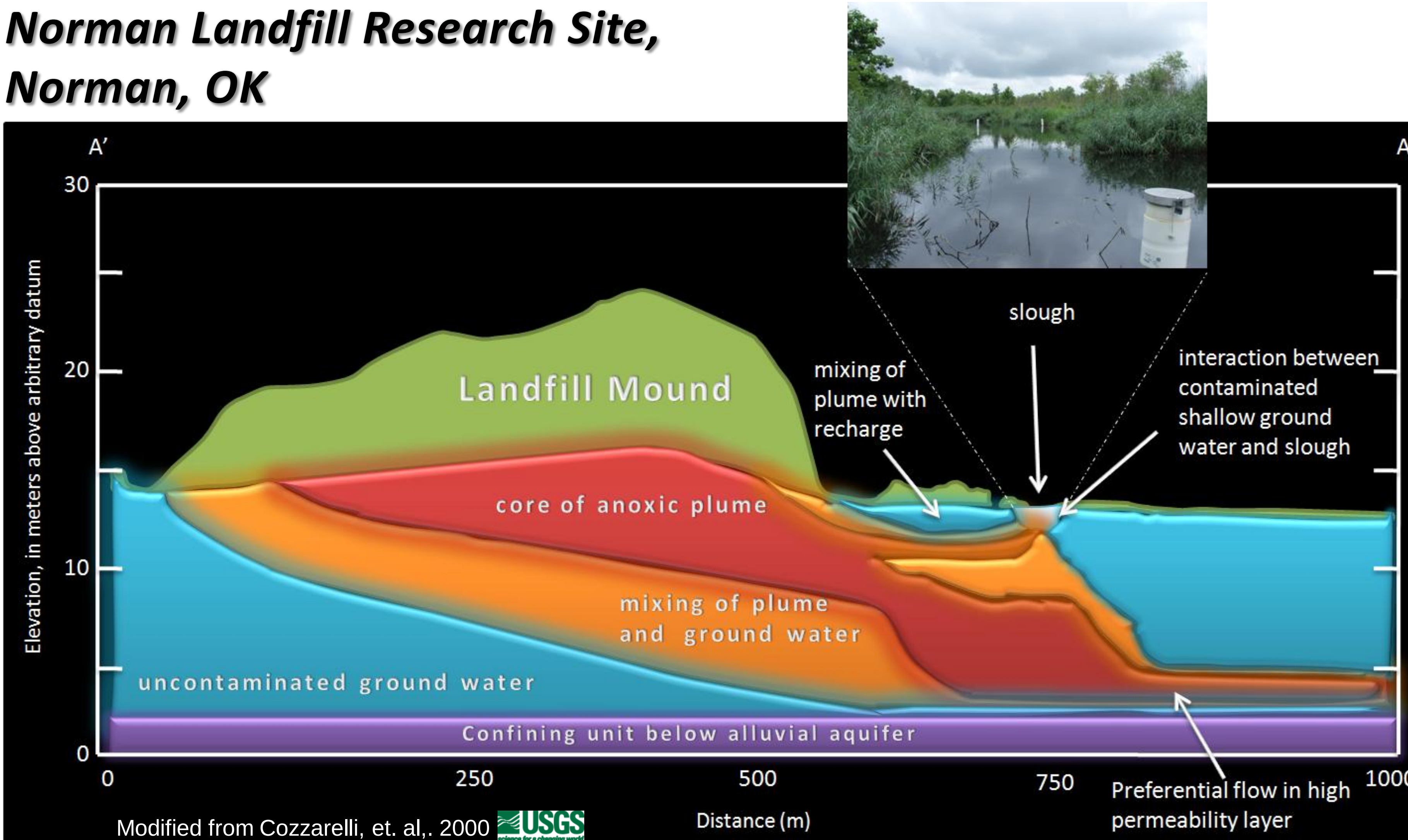
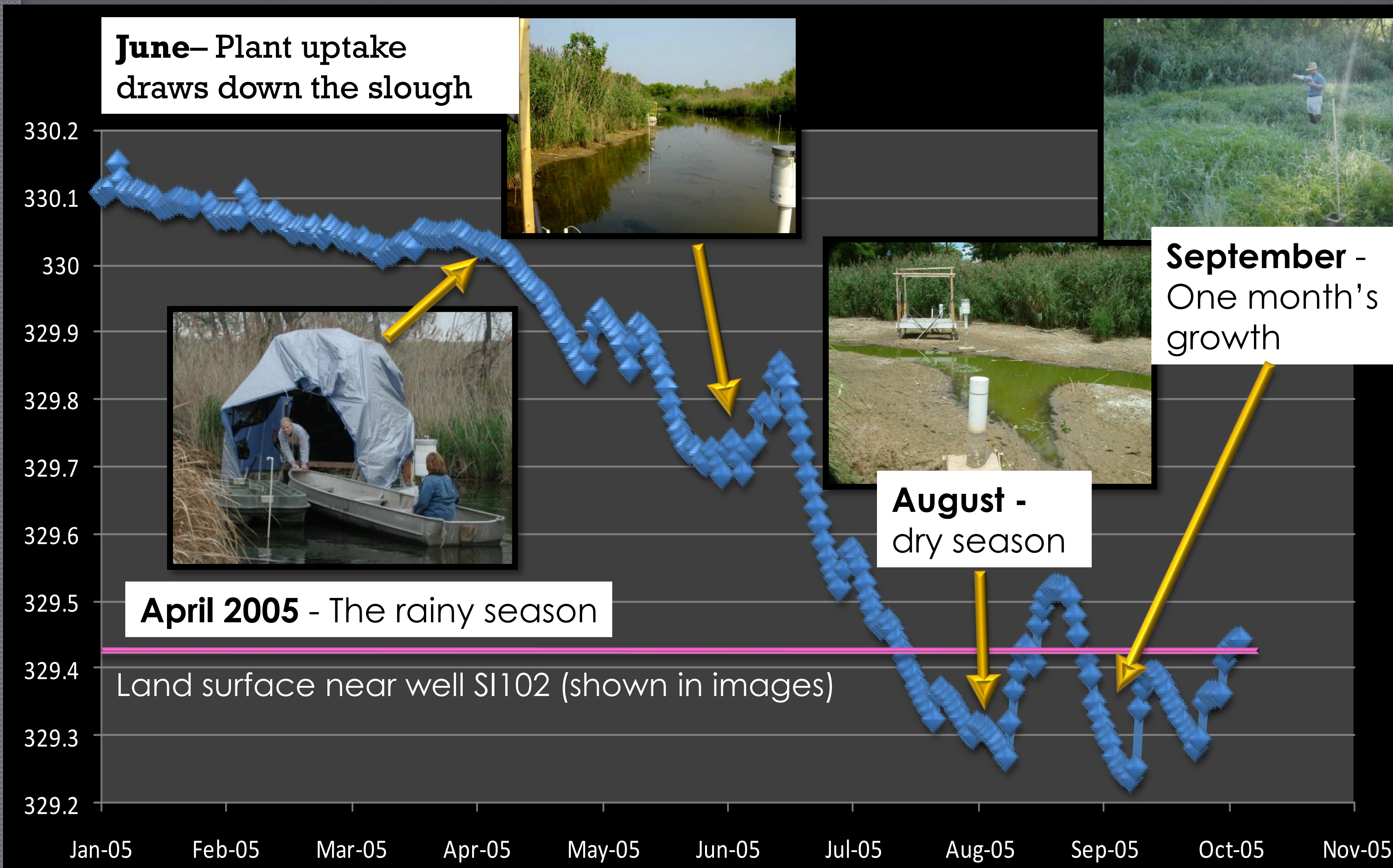


Conceptual model of transport and reactions zones at the Norman Landfill

Temporal Variability

Daily Slough Water Level- Elevation in Meters Above Sea Level

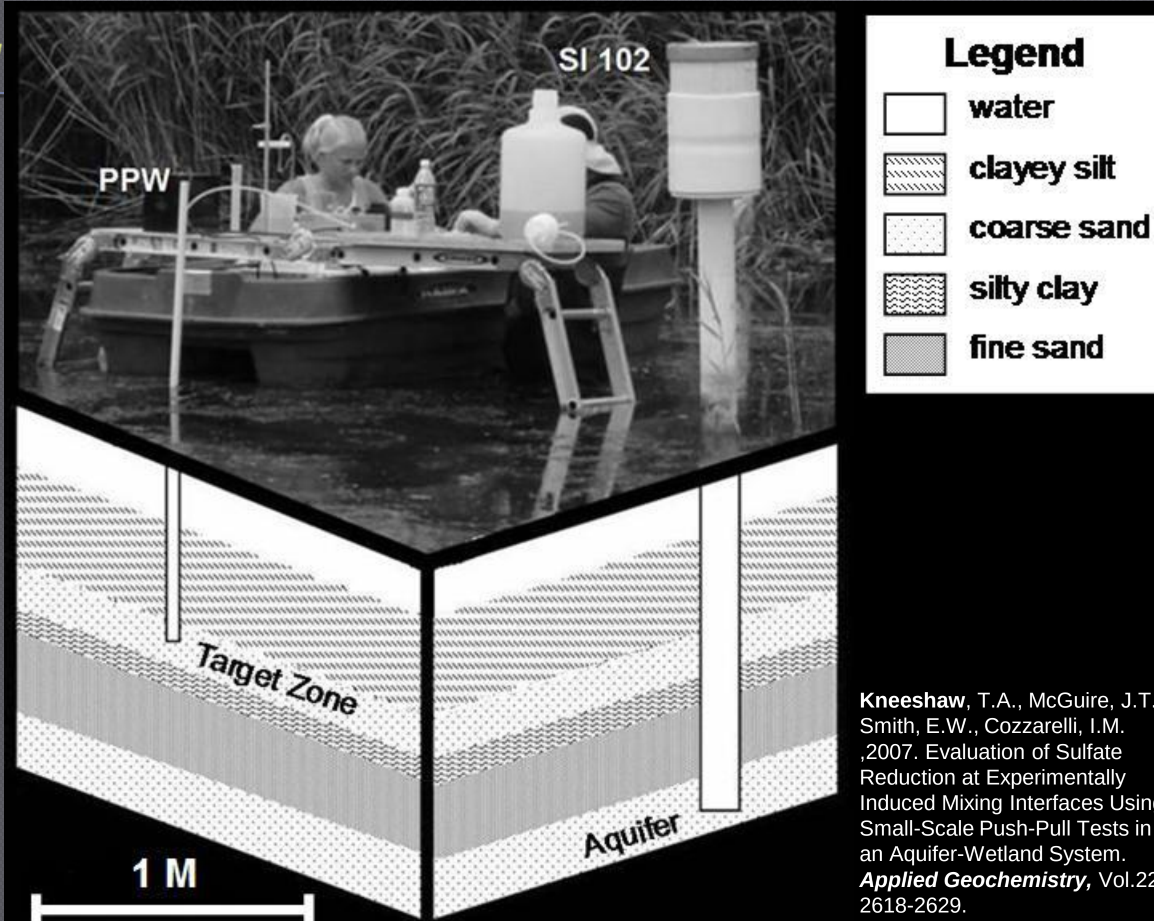


In-Situ Rate Studies

TEST SOLUTION- "PUSH" PHASE

- Extracted water from aquifer

- Augmented with combinations of ***electron acceptors*** (ex. SO_4^{2-}), ***electron donors*** (ex. acetate) and a **tracer** (ex. bromide)

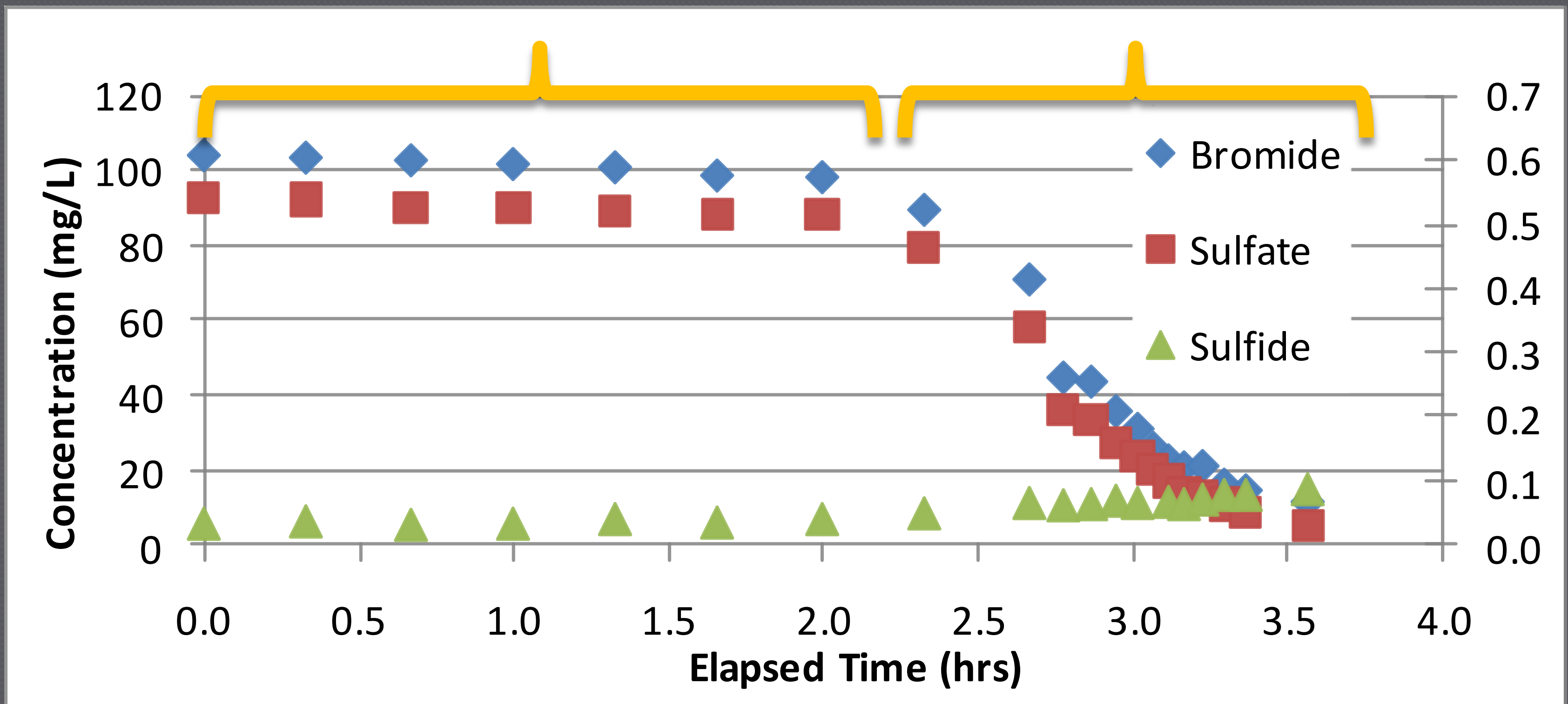


Kneeshaw, T.A., McGuire, J.T., Smith, E.W., Cozzarelli, I.M. ,2007. Evaluation of Sulfate Reduction at Experimentally Induced Mixing Interfaces Using Small-Scale Push-Pull Tests in an Aquifer-Wetland System. ***Applied Geochemistry,*** Vol.22, 2618-2629.

GOAL: **Create a mixing interface and measure rates of reactions initiated**

Data Analysis

1. Little Mixing **2. Mixing**



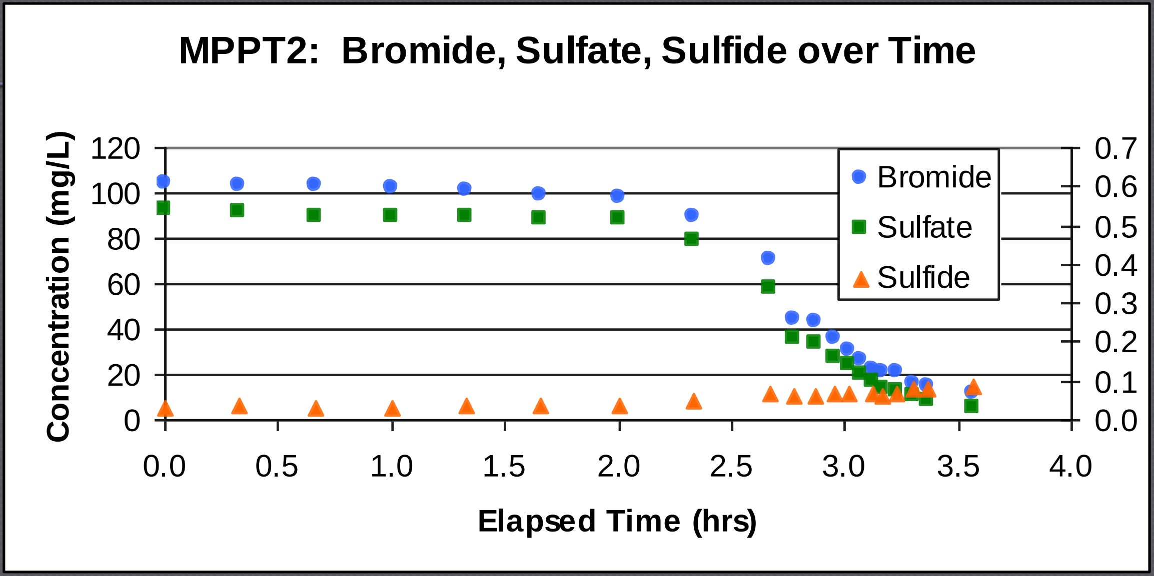
MPPT2: Bromide, Sulfate, Sulfide over Time

Kneeshaw, T.A., McGuire, J.T., Smith, E.W., Cozzarelli, I.M., 2007. Evaluation of Sulfate Reduction at Experimentally Induced Mixing Interfaces Using Small-Scale Push-Pull Tests in an Aquifer-Wetland System. ***Applied Geochemistry,*** Vol.22, 2618-2629.

Rate Determination

Assume first-order

$$C_r(t) = C_r^o e^{-kt}$$



Breakthrough curve then is given by:

$$C_r(t^*) = \frac{C_{tr}(t^*)}{kt_{inj}}\left[e^{-kt} - e^{-k(t_{inj}-t^*)}\right]$$

Rewritten:

$$\ln\left(\frac{C_r(t^*)}{C_{tr}(t^*)}\right) = \ln\left(\frac{1-e^{-kt_{inj}}}{kt_{inj}}\right) - kt^*$$

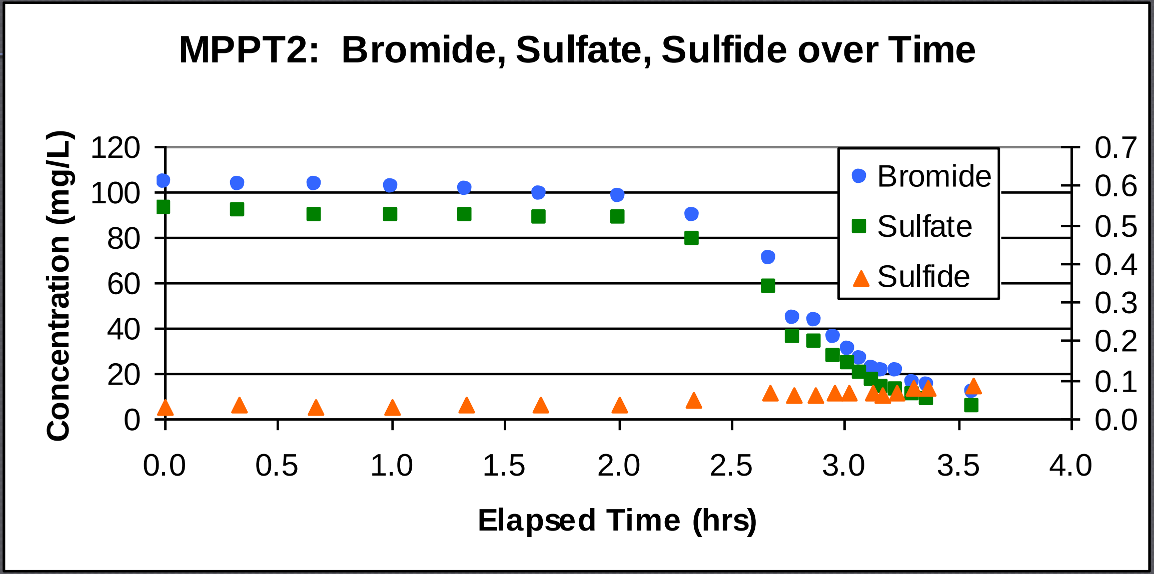
** After Snodgrass and Kitanidis, 1998*

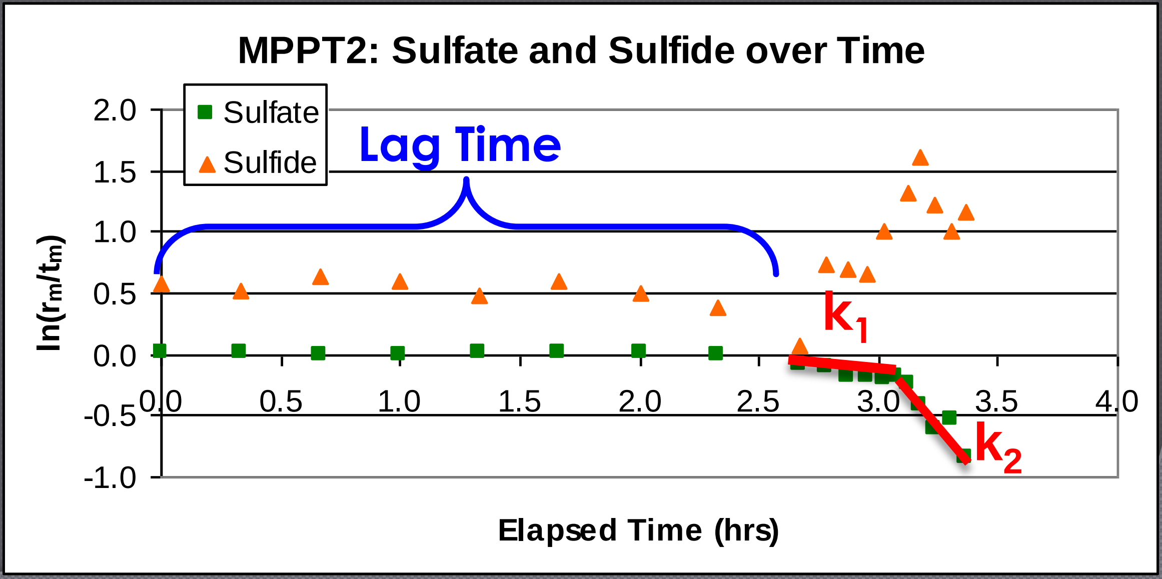
➡**This suggests that a plot of *ln(C_r/C_{tr})* versus time yields a straight line with a slope of *k*.**

Kneeshaw, T.A., McGuire, J.T., Smith, E.W., Cozzarelli, I.M., 2007 Evaluation of Sulfate Reduction at Experimentally Induced Mixing Interfaces Using Small-Scale Push-Pull Tests in an Aquifer-Wetland System. ***Applied Geochemistry,*** Vol.22, 2618-2629.

Rate Determination

- Rates comparable to other studies
- Lag Time? ~2.5 hours





k_1=0.3128 (hr^{-1}) R^2=0.9593

k_2=1.8947 (hr^{-1}) R^2=0.8971

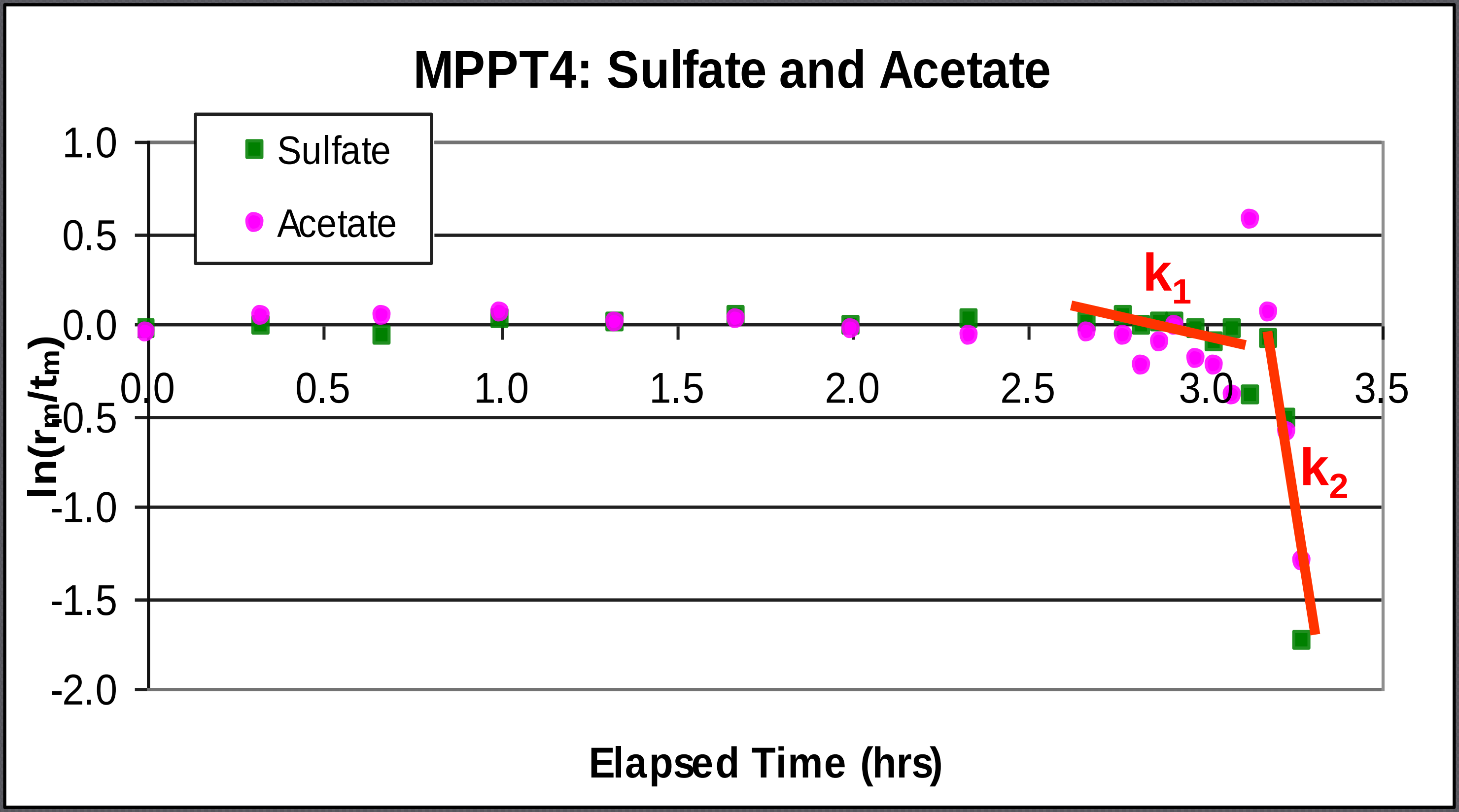
In-Situ Rate Studies

Sample Data

✓ acetate did NOT eliminate lag phase (~2.5 hours)

$k_1 = 0.2055$ (hr^{-1})
$R^2 = 0.4541$

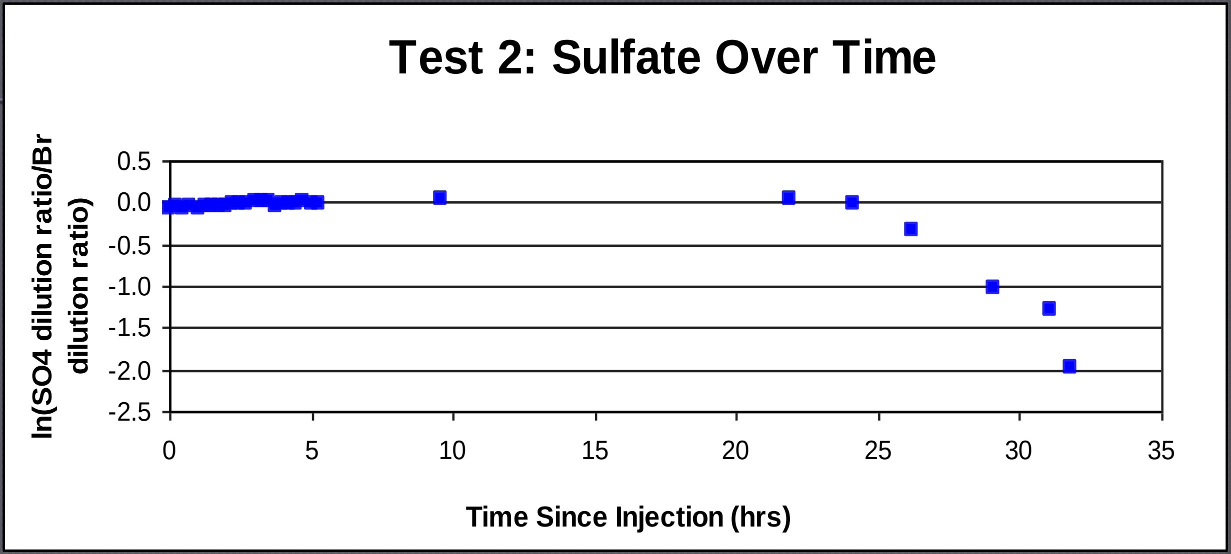
$k_2 = 7.07$ (hr^{-1})
$R^2 = 0.6485$

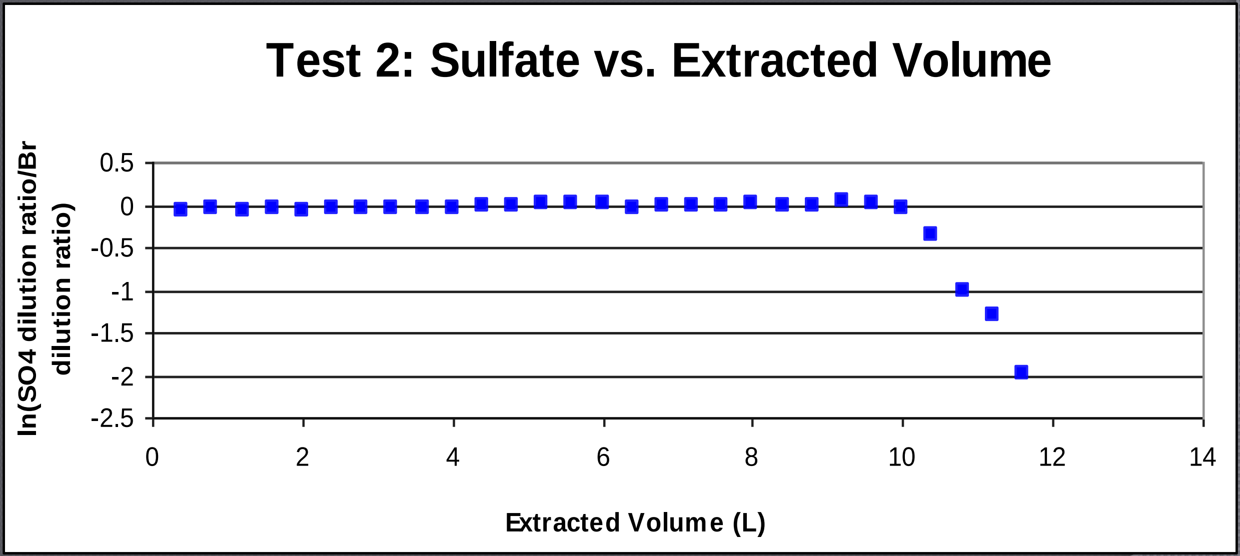


In-Situ Rate Studies

Long Test

- 10 L injected
- TOTAL TIME=
  - 34 hours
- LAG TIME=
  ~ 25 hours!

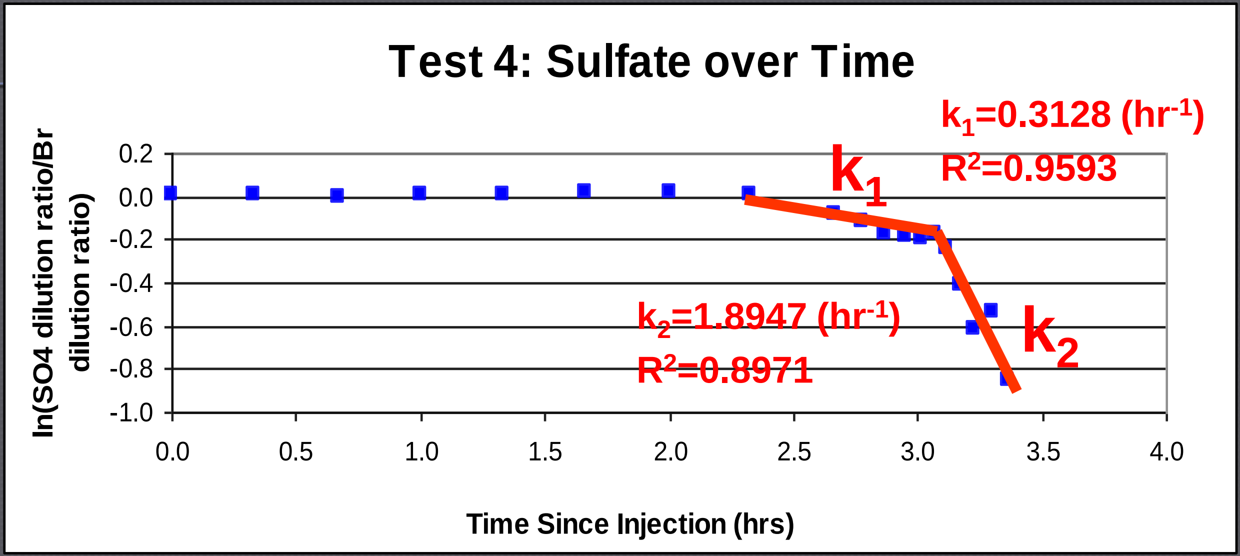


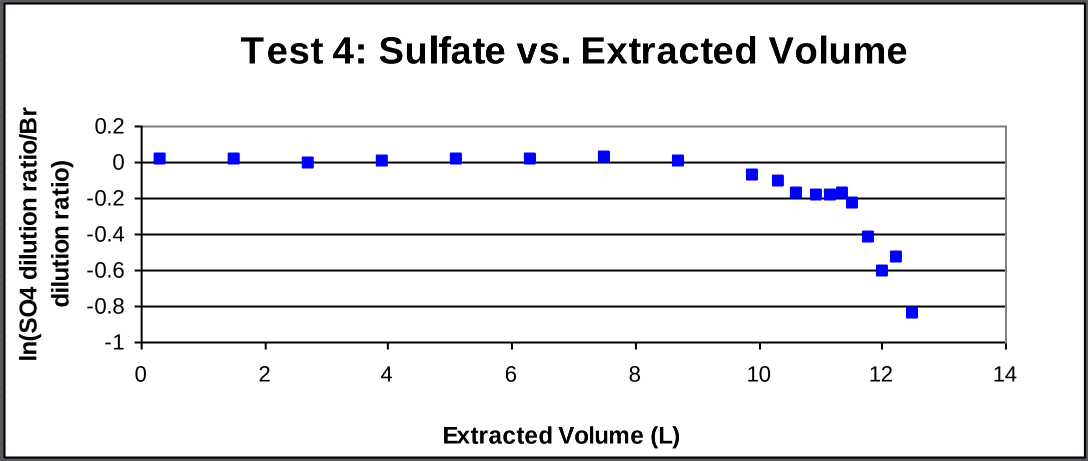


In-Situ Rate Studies

Short Test (repeated)

- 10 L injected
- TOTAL TIME=
  - 3.4 hours
- LAG TIME=
  ~ 2.5 hours

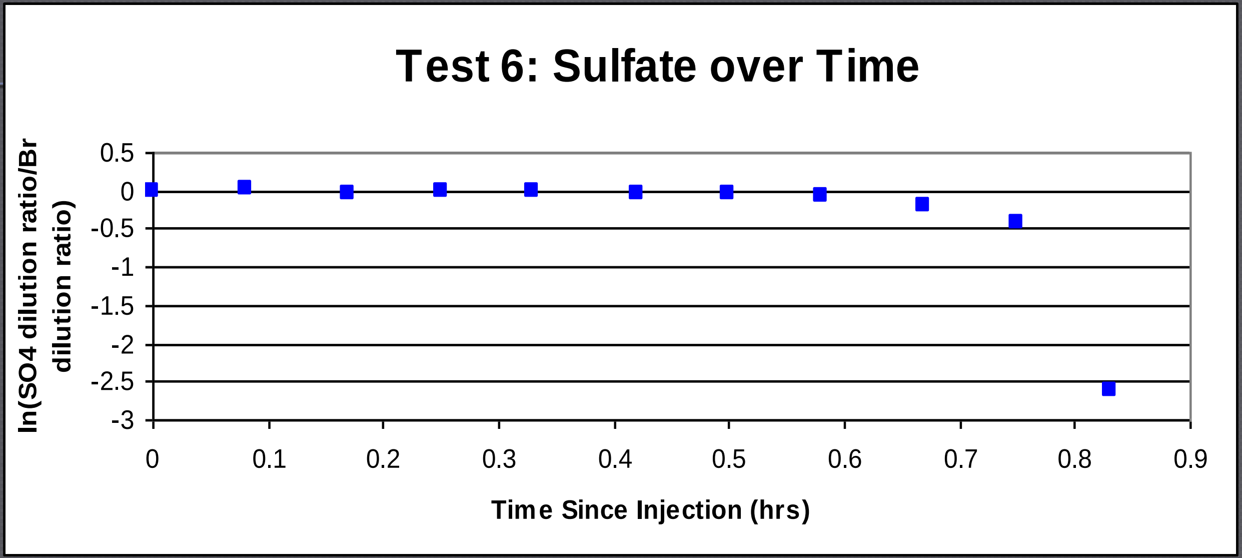


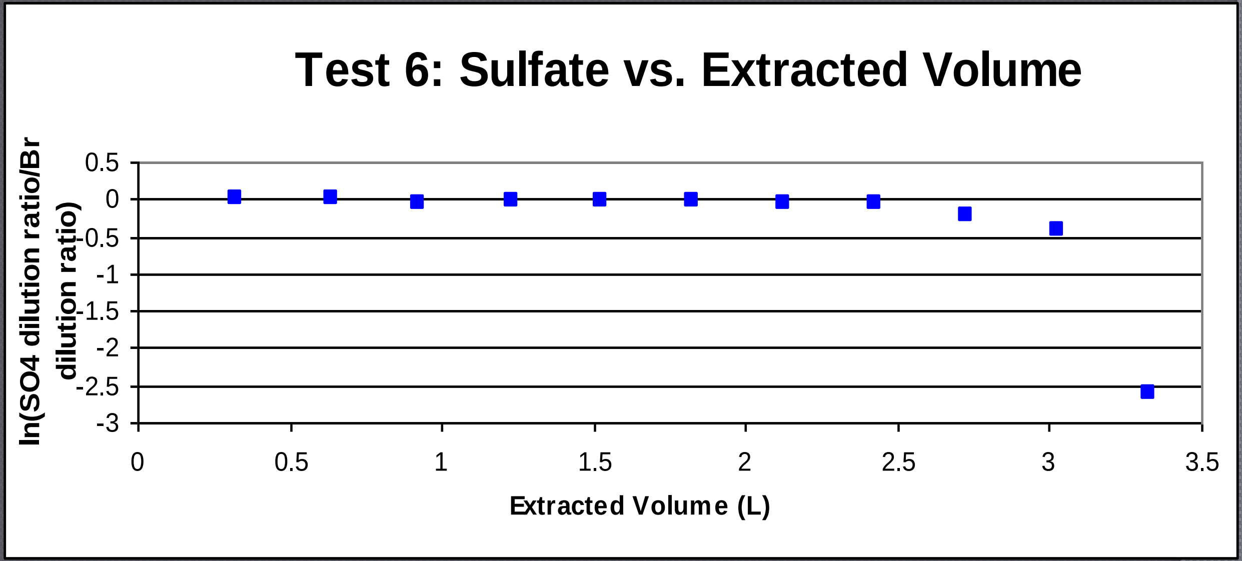


In-Situ Rate Studies

Smaller Volume

- 3 L injected
- TOTAL TIME=
  - < 1hr
- LAG TIME=
  ~ 0.6 hours





Questions

If the rate is a function of space what do our estimates versus time really mean?

A New Approach

Eliminate the mixing interface and measure the resulting reaction rates directly

How?

NOGEEs

(Native Organism Geochemical Experimental Enclosures)

Goal:

1) Trap a native microbial population
2) Isolate the test chamber from the surrounding environment
3) Introduce geochemical solutions
4) Measure the resulting reaction rates

T.A. Kneeshaw, "Evaluation of Kinetic Controls on Sulfate Reduction in a Contaminated Wetland-Aquifer System," PhD Dissertation, Texas A&M University, College Station, TX, 2008.

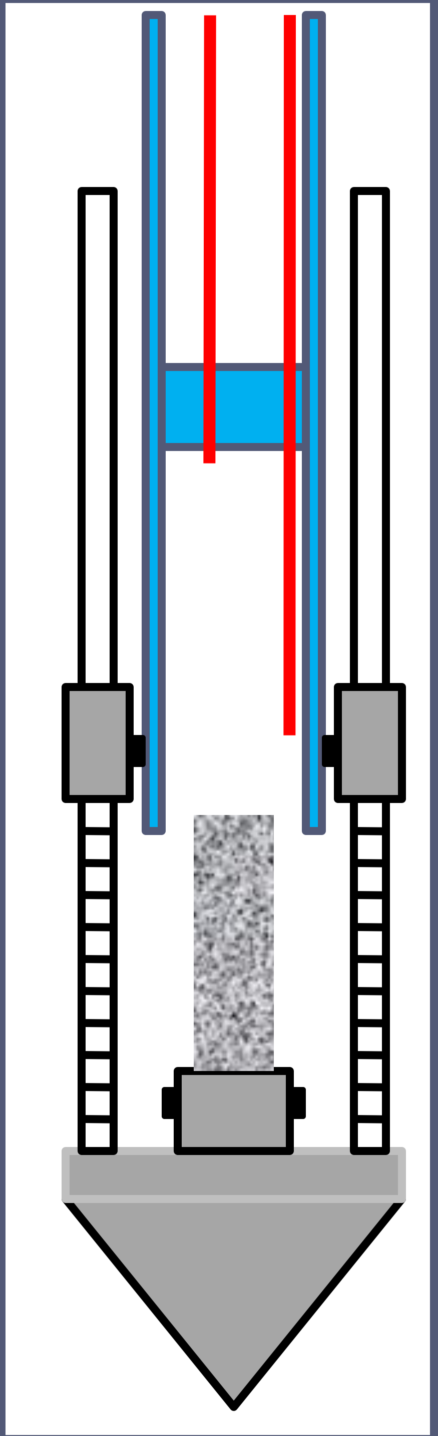
NOGEE Design

Step 1: Equilibration with surrounding environment (4-6 weeks)

Step 2: Inner pipe is lowered

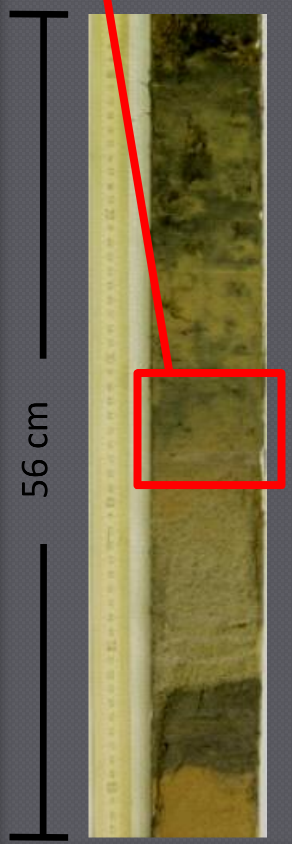
Step 3: Introduction and removal of test solution

Step 4: Measure the resulting reaction rates

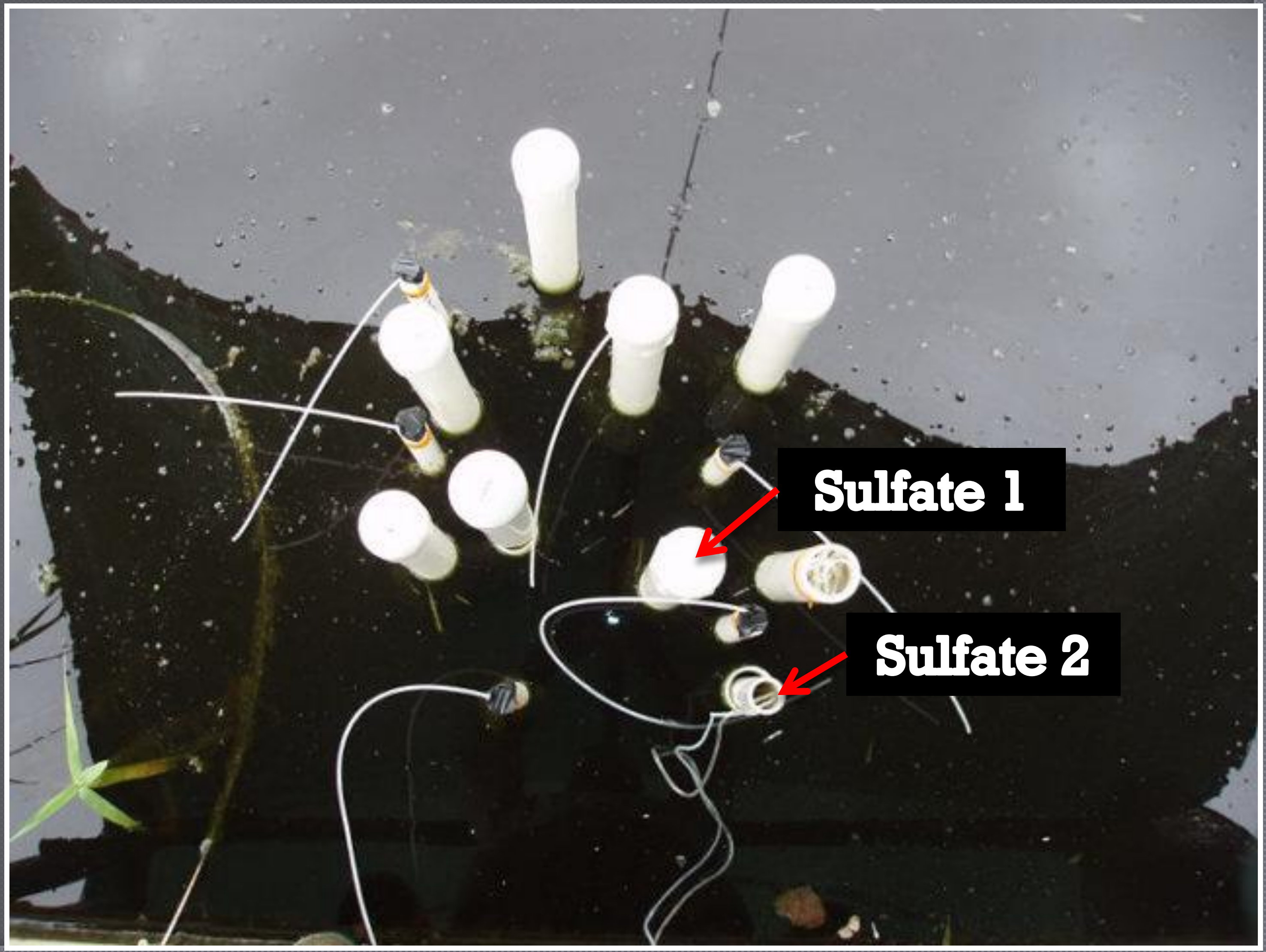


NOGEE Placement

Approximate depth of NOGEE membrane



Plan view of NOGEEs



NOGEE Experiment

Test solution:

-landfill-leachate contaminated aquifer water
-SO_4^{2-} (~100 mg/L)
-lactate and acetate
-Br^-
-Introduced 5 times over 11 days

Samples:

Geochemistry

- ***field and laboratory techniques***

Results-Rate Data

Rate Data

Sulfate reduction rates increased after the first sampling event (48 hours exposed to test solution)

Sampling Event	Sulfate NOGEE 1 Rate ($mg/l\ hr^{-1}$)	Sulfate NOGEE 2 Rate ($mg/l\ hr^{-1}$)
1	0.829	1.192
2	1.598	1.628
3	1.748	1.658
4	1.480	1.211
5	1.659	1.426

T.A. Kneeshaw, "Evaluation of Kinetic Controls on Sulfate Reduction in a Contaminated Wetland-Aquifer System," PhD Dissertation, Texas A&M University, College Station, TX, 2008.

Conclusions

- In situ experiments like those discussed here are important tools for evaluating the linked microbiological and geochemical *controls* on reaction rates in complex natural systems.

- Experiments are simple to conduct but we need MANY studies to tease out kinetic controls on important reactions.

- Look at controls on same reaction in different environments.

- Continue to work towards the ultimate goal of providing rates that can be used to predict chemical fate and transport in dynamic natural environments.

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Thank You