IN-SITU CHARACTERIZATION & REMEDIATION OF CONTAMINATED AQUIFERS

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OUTLINE

- Background

- Objectives

- Groundwater Velocity $\left(\vec{v} = \frac{\Delta x}{\Delta t}\right)$

- Uranium Immobilization $(U^{6+} \rightarrow U^{4+})$

- Nitrate Reduction $(NO_3^- \rightarrow NO_2^-)$
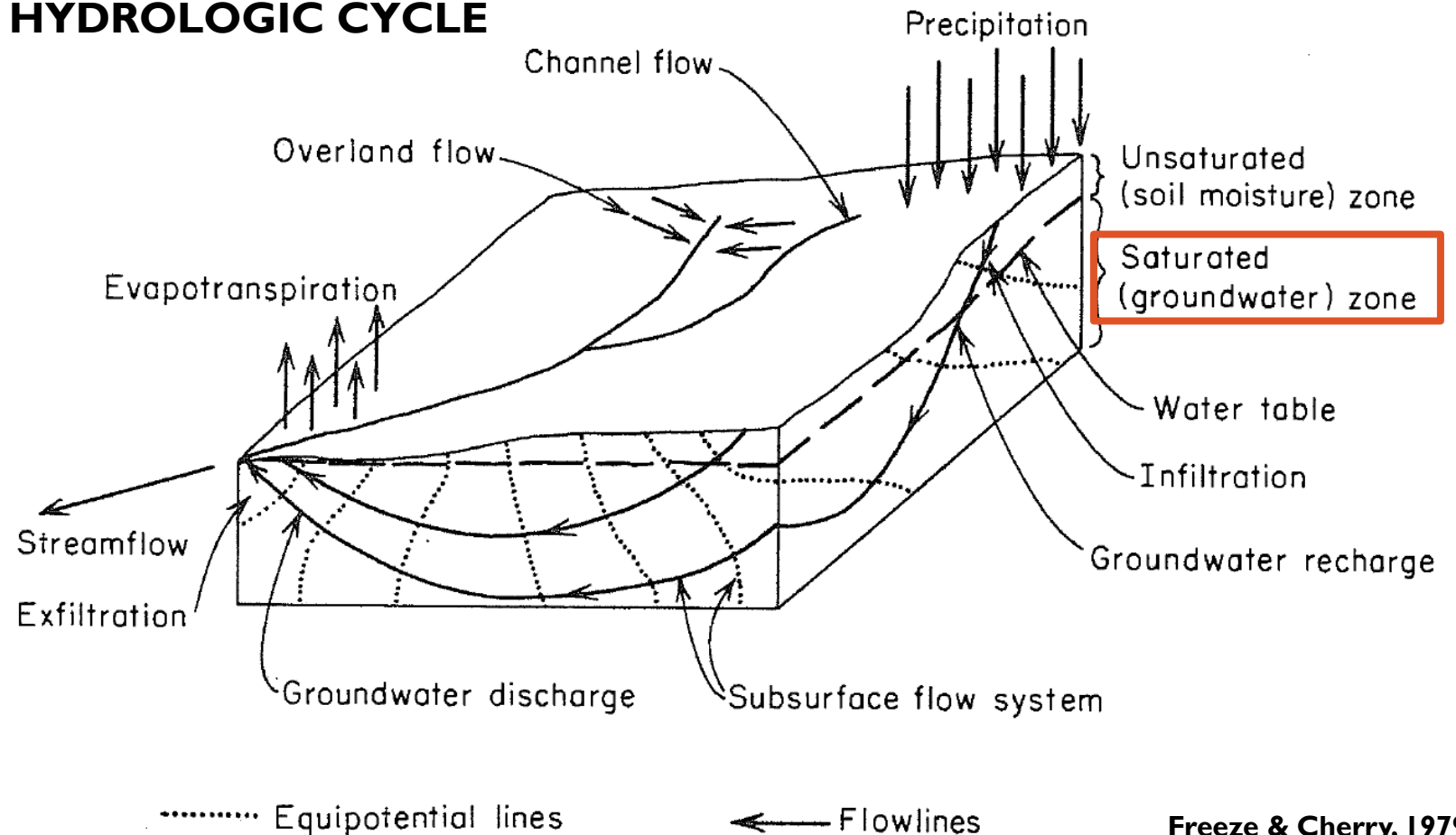
- Future Research Throughout

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GROUNDWATER FACTS

- 30% world freshwater
- In the USA:
- 38% use it for drinking
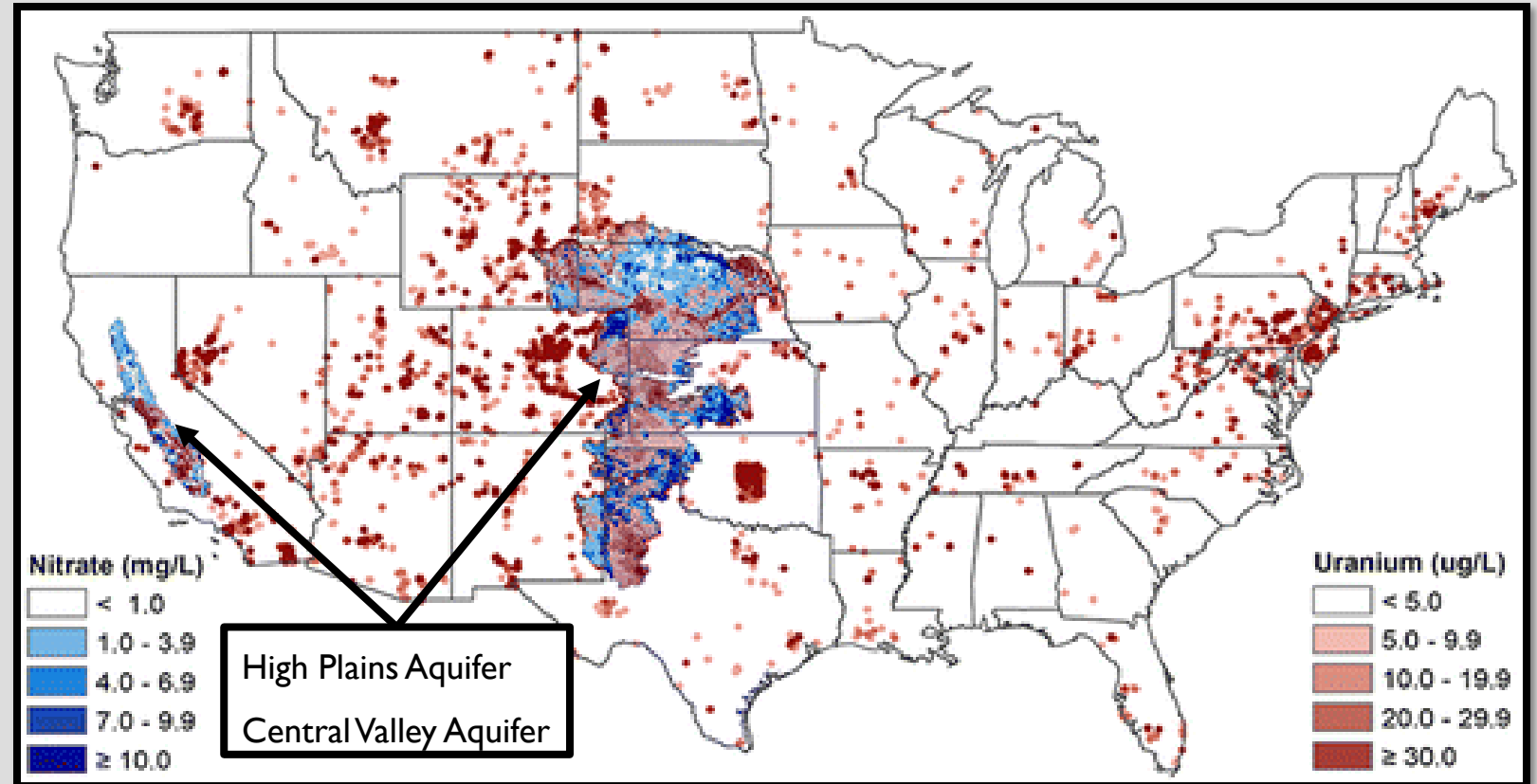- Irrigation #1 user
- You can't see it!!!

HYDROLOGIC CYCLE

Freeze & Cherry, 1979
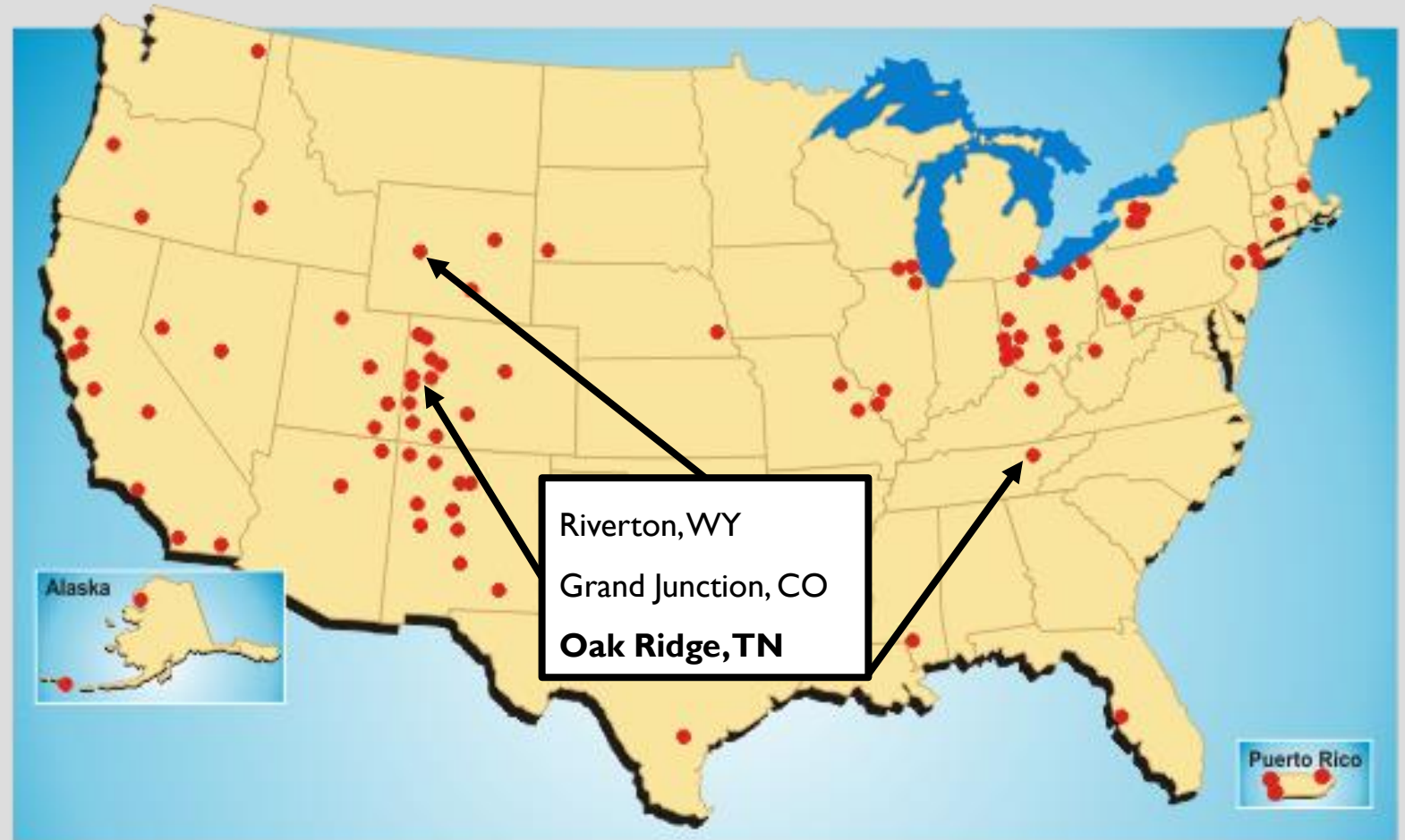
GROUNDWATER CONTAMINATION

- Impact major aquifers

- Natural & human activity

- Microorganisms (E.coli)

- Radionuclides (**Uranium**)

- Heavy metals (Chrome)

- Fertilizers (**Nitrate**)

- Emerging (1,4-Dioxane)

- Emerging (Nanomaterial)

Nitrate (mg/L)
- < 1.0
- 1.0 - 3.9
- 4.0 - 6.9
- 7.0 - 9.9
- ≥ 10.0

High Plains Aquifer

Central Valley Aquifer

Uranium (ug/L)
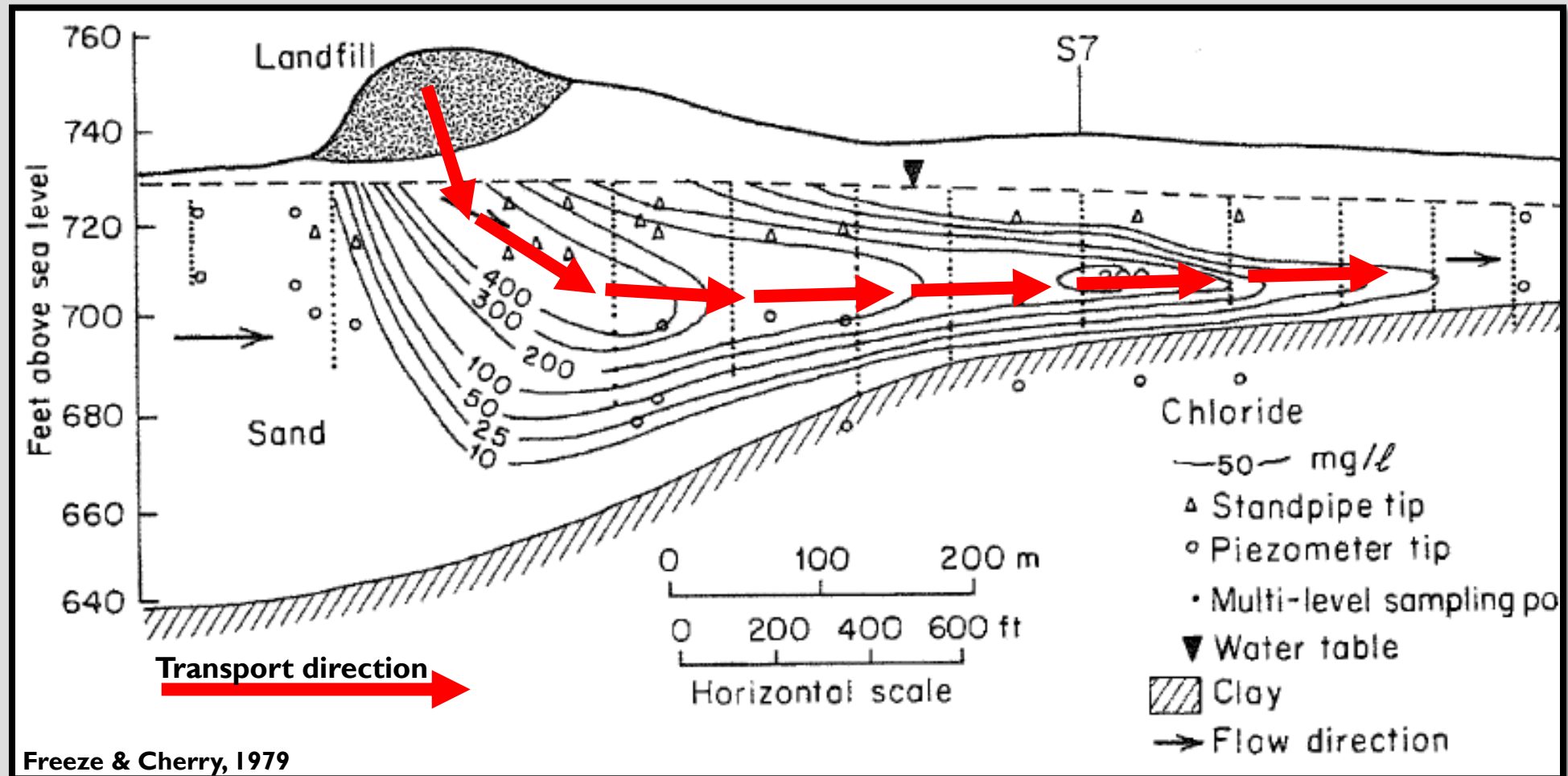- < 5.0
- 5.0 - 9.9
- 10.0 - 19.9
- 20.0 - 29.9
- ≥ 30.0

Nolan & Weber, 2015 *ES&T*

GROUNDWATER CONTAMINATION

- DOE Legacy Management
- Former nuclear sites (94)
- **Uranium**
- Technetium
- Vanadium
- **Nitrate**
- Mercury
- Riverton, WY
- Grand Junction, CO
- **Oak Ridge, TN**

Riverton, WY

Grand Junction, CO

Oak Ridge, TN

Alaska

Puerto Rico

https://www.energy.gov/lm/sites/lm-sites

GROUNDWATER FLOW & CONTAMINANT TRANSPORT (MACRO)

Freeze & Cherry, 1979

GROUNDWATER FLOW & CONTAMINANT TRANSPORT (MICRO)

- Transport governed by:

1. **Advection ($\vec{v}$)**

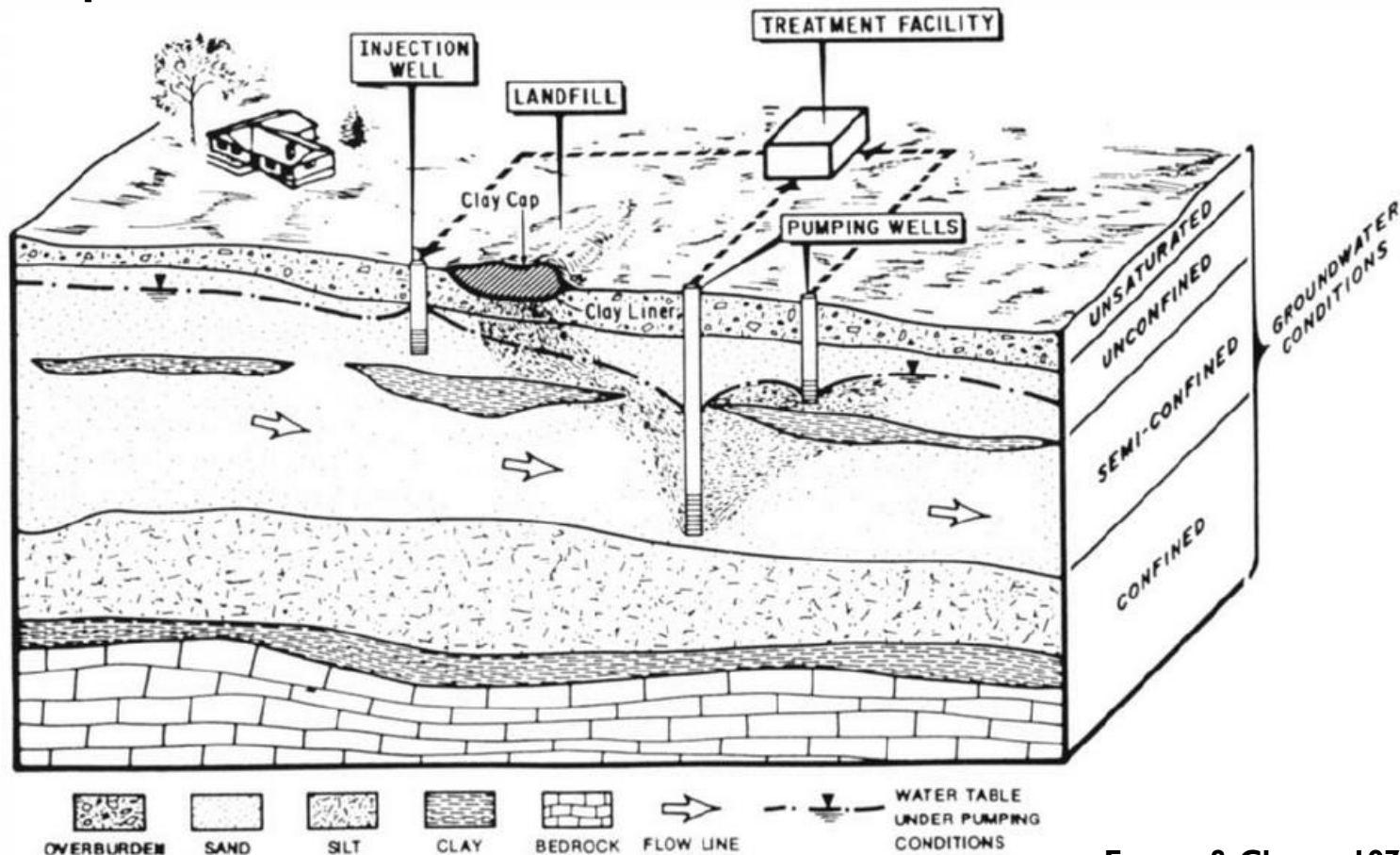2. Mechanical dispersion (α)

3. Molecular diffusion (D)

Advection ($\vec{v}$)

Diffusion (D)

Dispersion (α)

Freeze & Cherry, 1979

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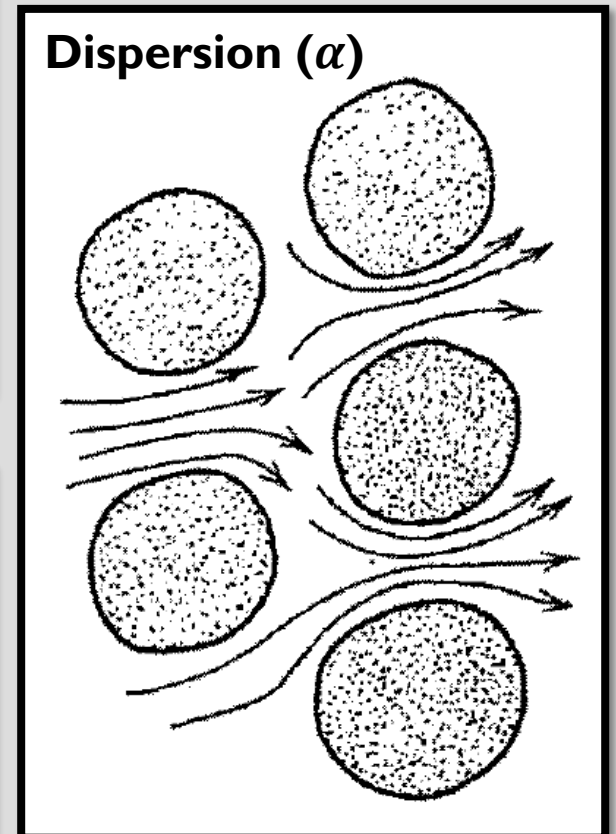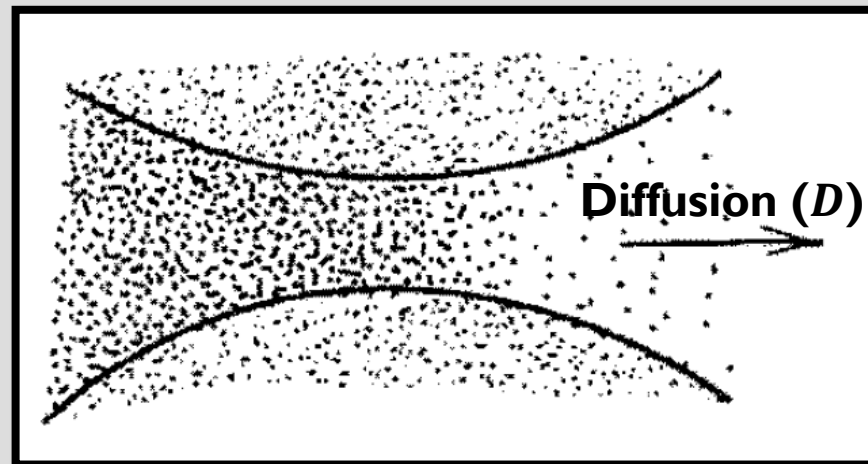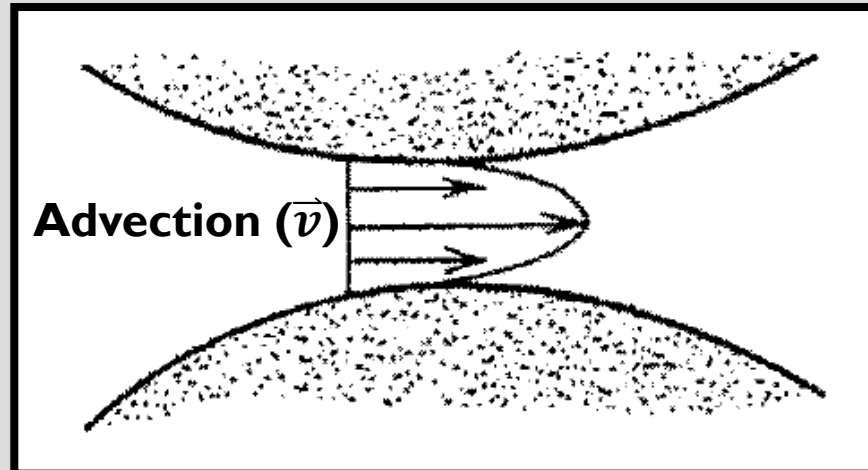
AQUIFER CHARACTERIZATION (STANDARD METHODS)

■ **Pump tests are common practice**
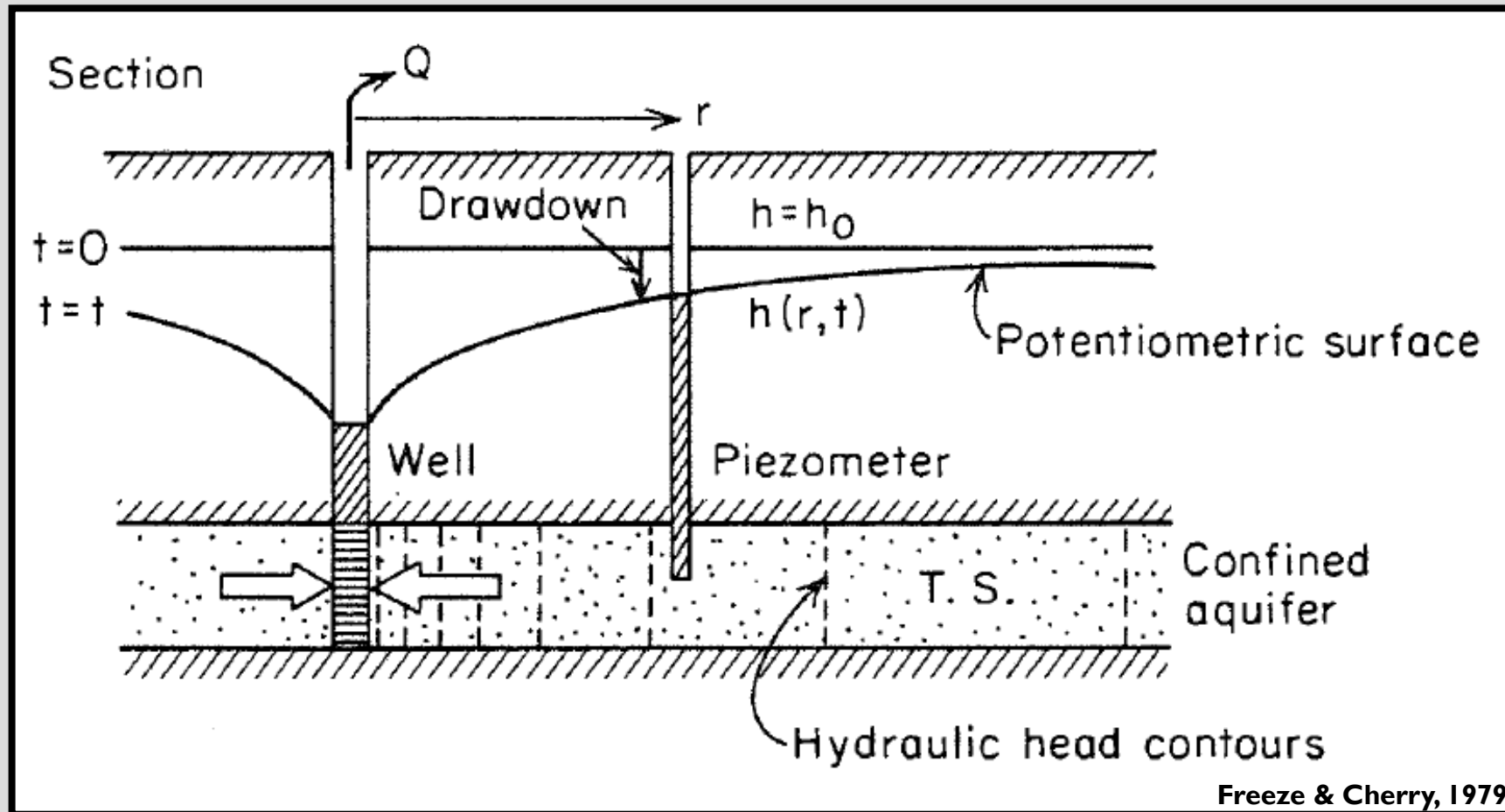
Freeze & Cherry, 1979

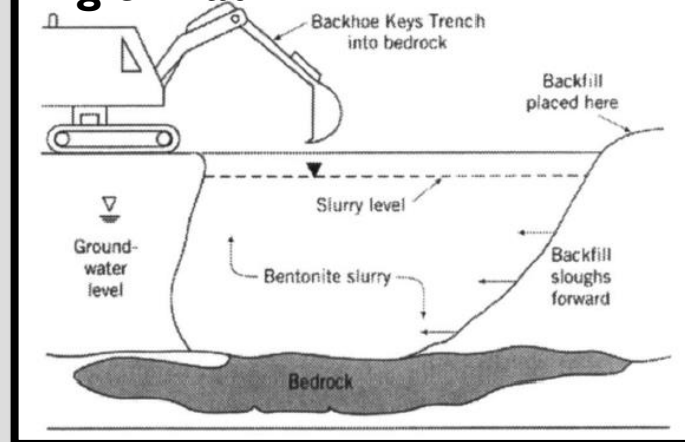# CONTAMINANT REMEDIATION (STANDARD METHODS)

Pump & Treat
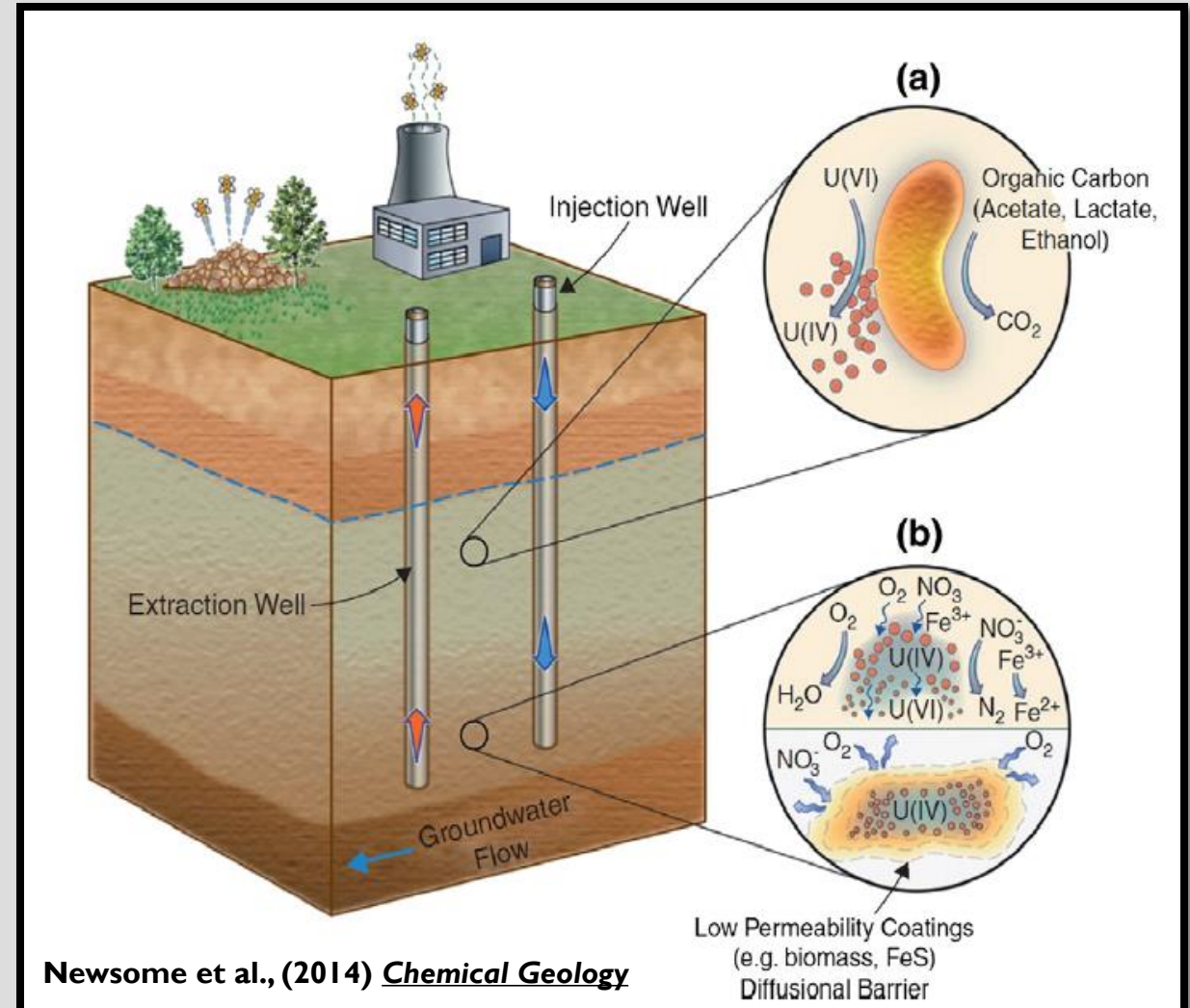

Freeze & Cherry, 1979

**Pump & Treat and Dig & Haul are standard practice**

Dig & Haul

HYDROGEOLOGY & ENVIRONMENTAL MICROBIOLOGY

- "The role of the infinitely small is infinitely powerful"
- Uranium immobilization ($U^{6+} \rightarrow U^{4+}$)
- Microbial mediated

Newsome et al., (2014) *Chemical Geology*

HYDROGEOLOGY & ENVIRONMENTAL MICROBIOLOGY

- "The role of the infinitely small is infinitely powerful"
- Nitrate reduction $(NO_3^- \rightarrow NO_2^-)$
- Microbial mediated
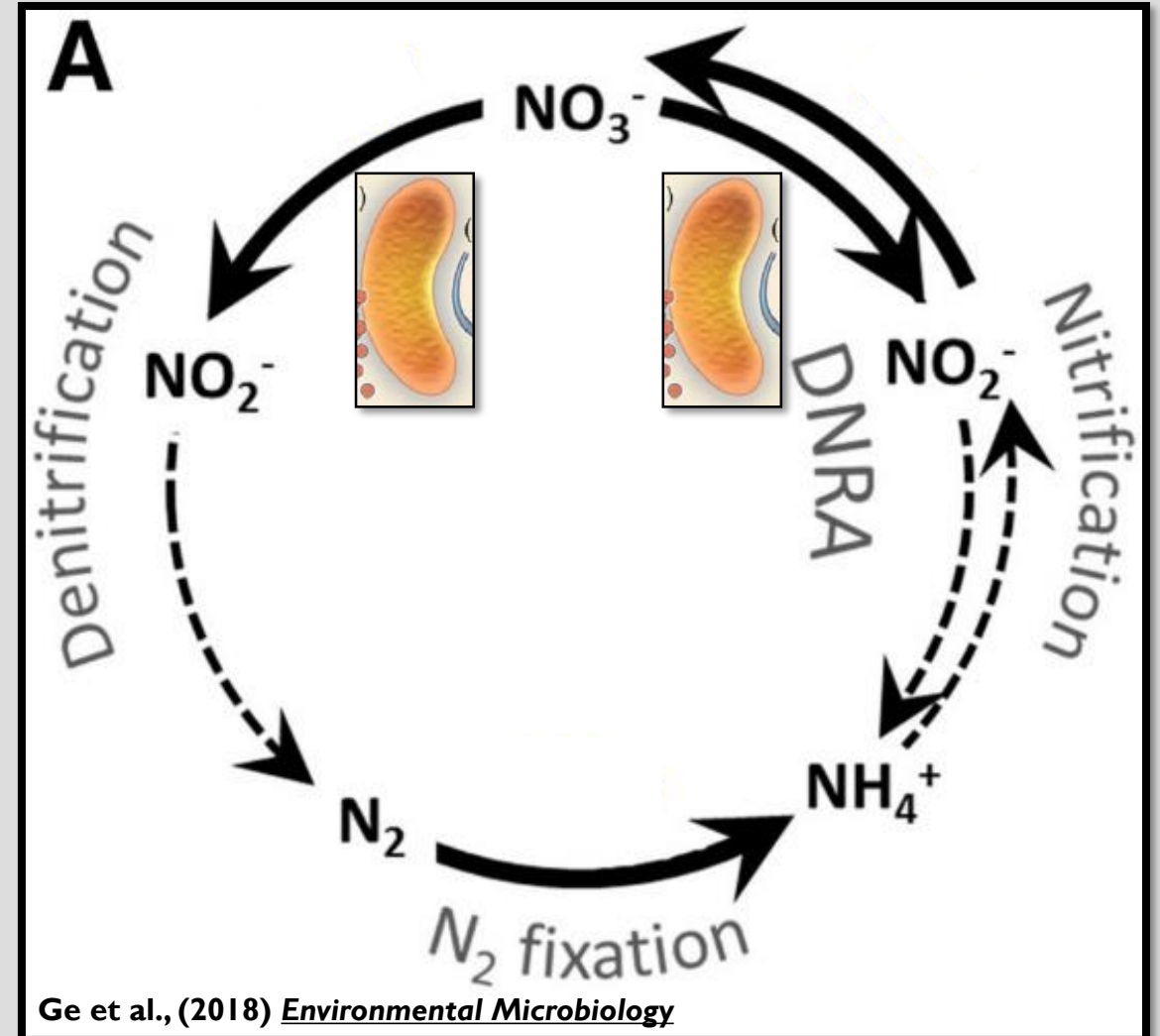
Ge et al., (2018) *Environmental Microbiology*

OUTLINE

- Background
- **Objectives**
- Groundwater Velocity $(\vec{v} = \frac{\Delta x}{\Delta t})$
- Uranium Immobilization $(U^{6+} \rightarrow U^{4+})$
- Nitrate Reduction $(NO_3^- \rightarrow NO_2^-)$
- Future Research Throughout

OBJECTIVES: BROAD

- Improve existing and develop new methods of in-situ characterization and remediation

- Incorporate microbiology to better understand and predict contaminant transport
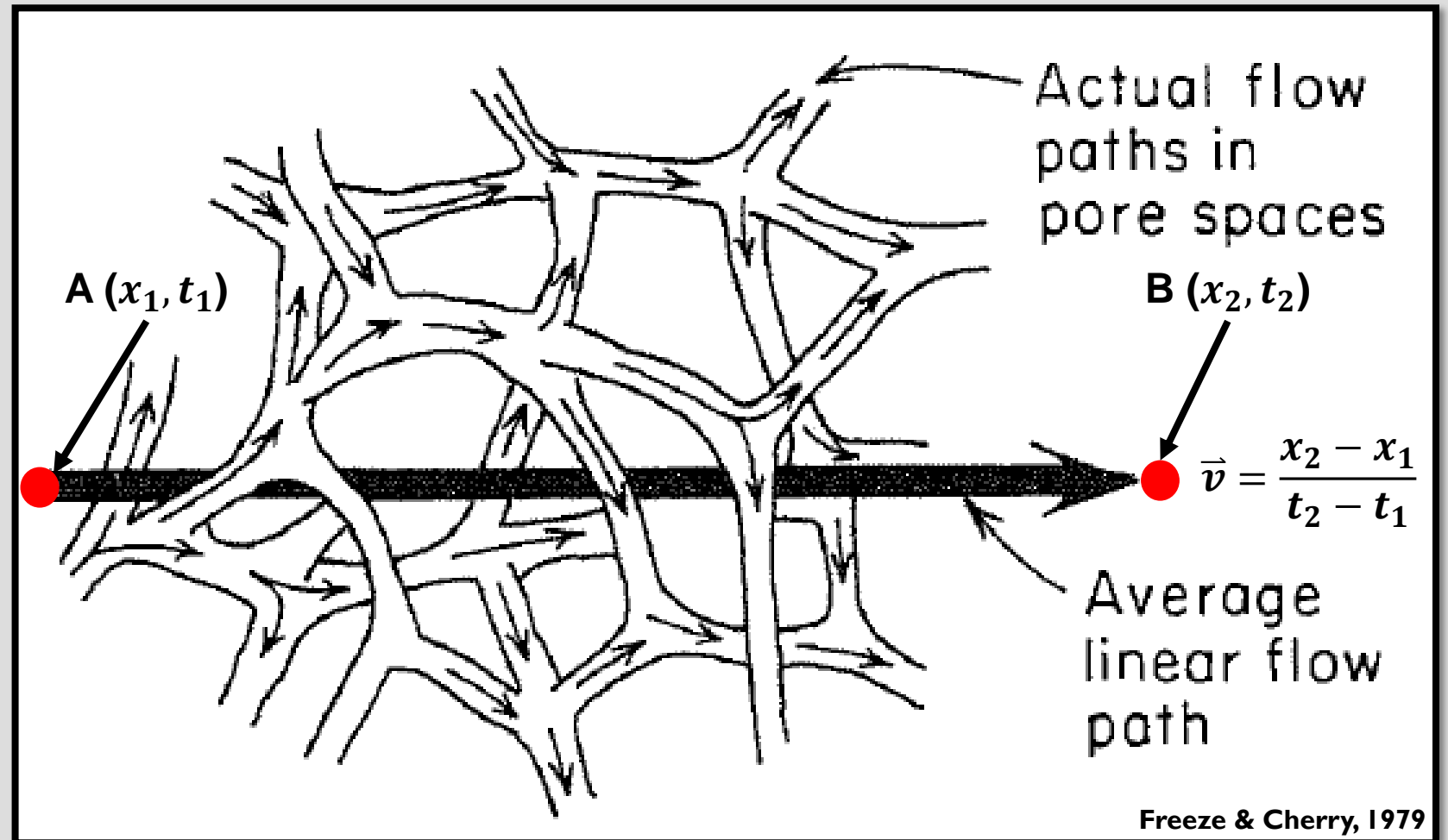
OBJECTIVES: SPECIFIC

- New method characterize groundwater velocity $\left(\vec{v} = \frac{\Delta x}{\Delta t}\right)$

- Improve method to immobilize uranium $(U^{6+} \rightarrow U^{4+})$

- Demonstrate molybdenum-limited bioreduction of nitrate $(NO_3^- \rightarrow NO_2^-)$

OUTLINE

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- Objectives

- **Groundwater Velocity ($\vec{v} = \frac{\Delta x}{\Delta t}$)**

- Uranium Immobilization ($U^{6+} \rightarrow U^{4+}$)

- Nitrate Bioreduction ($NO_3^- \rightarrow NO_2^-$)

- Future Research Throughout

GROUNDWATER VELOCITY ($\vec{v}$)

- **"Average rate water moves between two points (A → B)"**
- **Why do we care?**
- **<u>Primary parameter of contaminant transport*</u>**
- ***= typically...**

A (x_1, t_1)

Actual flow paths in pore spaces

B (x_2, t_2)

$$\vec{v} = \frac{x_2 - x_1}{t_2 - t_1}$$

Average linear flow path
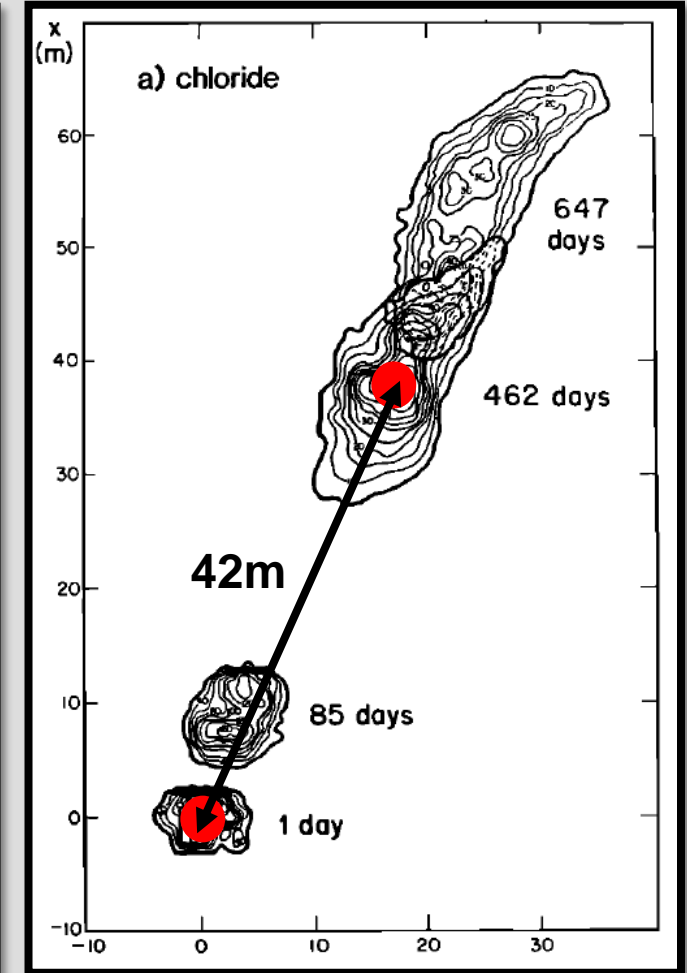
Freeze & Cherry, 1979

MULTI-WELL NATURAL-GRADIENT

- **Gold standard for $\vec{v}$**
- **Inject non-rxn tracer Cl⁻**
- **Monitor Cl⁻ transport**
- **Travel distance Δx**
- **Travel time Δt**
- $\vec{v} = \dfrac{\Delta x}{\Delta t}$
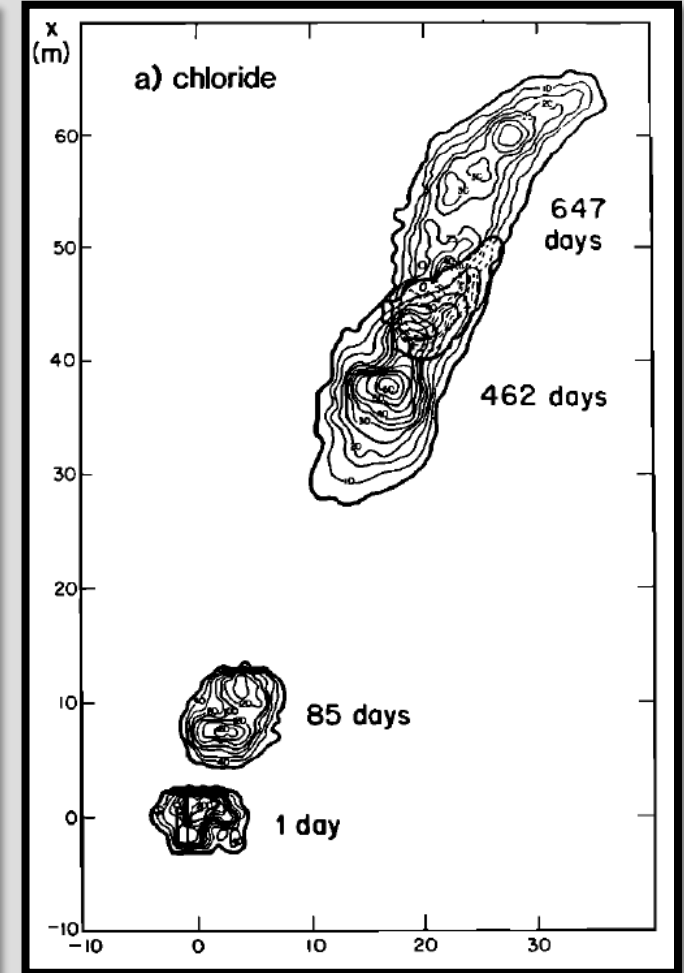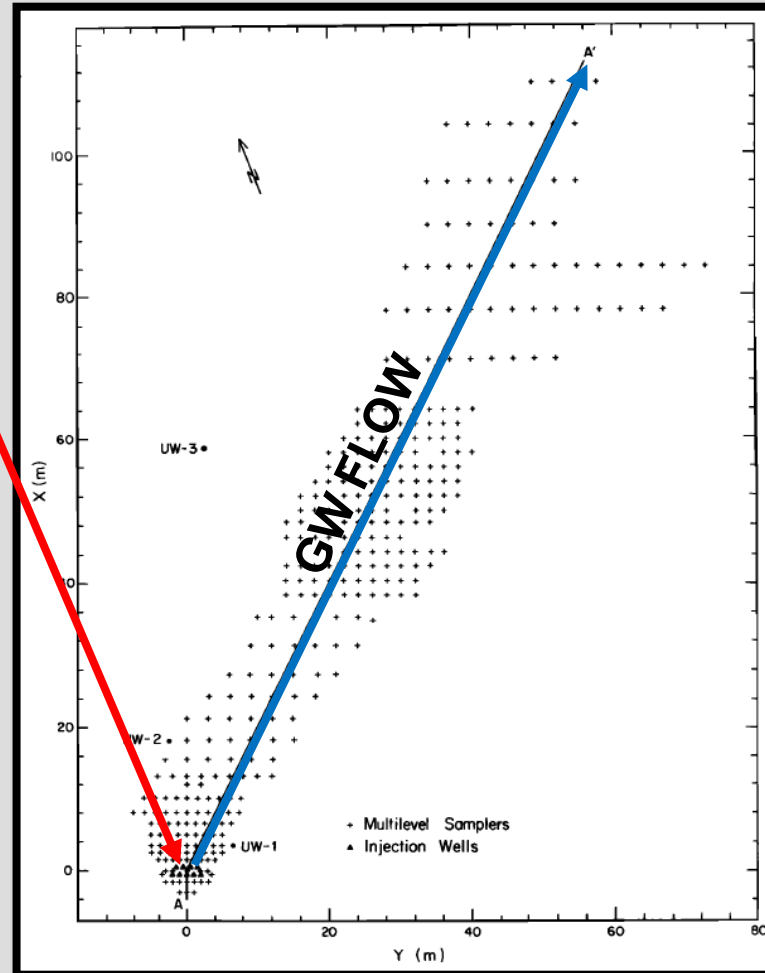
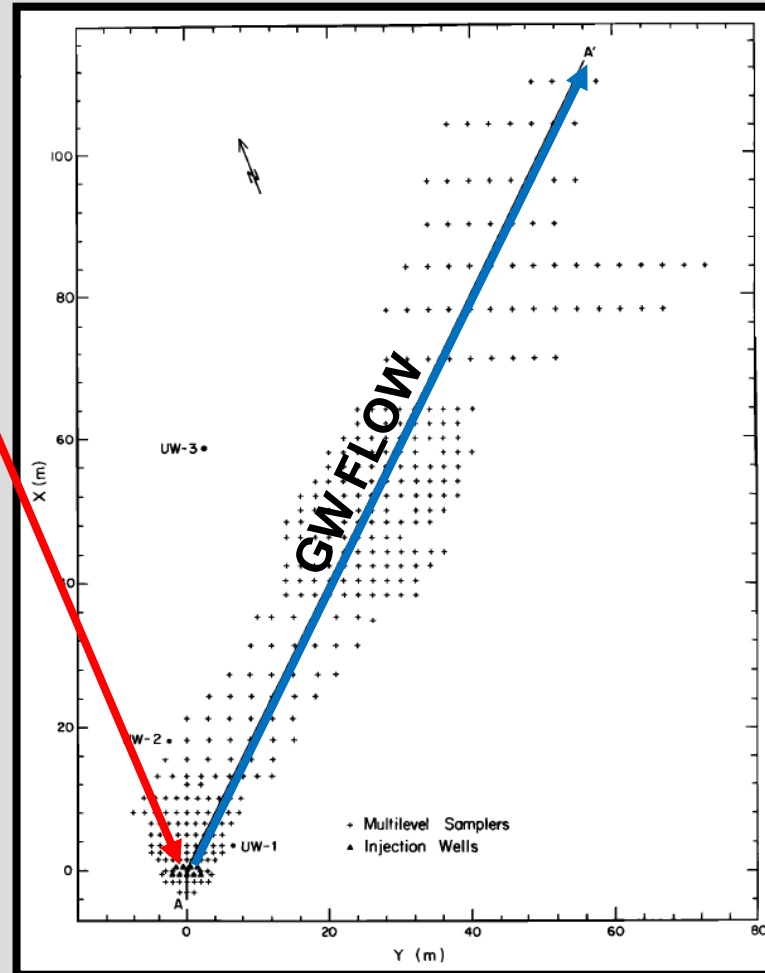**Mackay et. al., (1986) _WRR_**

MULTI-WELL NATURAL-GRADIENT

- **Gold standard for $\vec{v}$**

- **Inject non-rxn tracer Cl⁻**

- **Monitor Cl⁻ transport**

- **Travel distance Δx**

- **Travel time Δt**

- $\vec{v} = \dfrac{\Delta x}{\Delta t} = \dfrac{42\ m}{461\ days} \approx \dfrac{0.1 m}{day}$

- **↑↑↑ time, \$\$\$, expertise**

a) chloride

647 days

462 days

42m

85 days

1 day

Mackay et. al., (1986) _WRR_

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RESEARCH QUESTION #1

- **Can a single well be used to characterize groundwater velocity quickly, cheaply, & easily?**

- Pros: Investigate the aquifer directly with non-rxn tracer (Br^-)

- Pros: Generate little to no wastewater

- In theory, yes…

- Single-well Injection-Drift Test

SINGLE-WELL INJECTION-DRIFT TEST (MODEL)

- **Injection phase**: forced-gradient, radial-divergent transport
- Assume: natural-gradient (dh/dx) transport is negligible vs. forced-gradient

dh/dx

Paradis et. al., (2019) *Groundwater* (In Review)
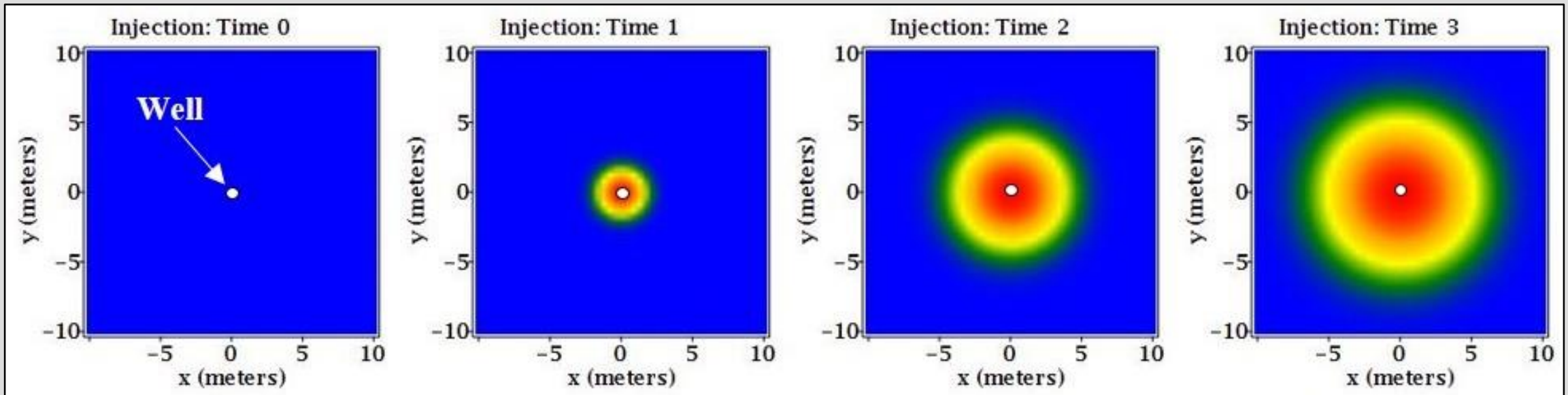
SINGLE-WELL INJECTION-DRIFT TEST (MODEL)

- **Drift phase**: natural-gradient, horizontal transport
- Assume: natural-gradient (dh/dx) transport is dominant
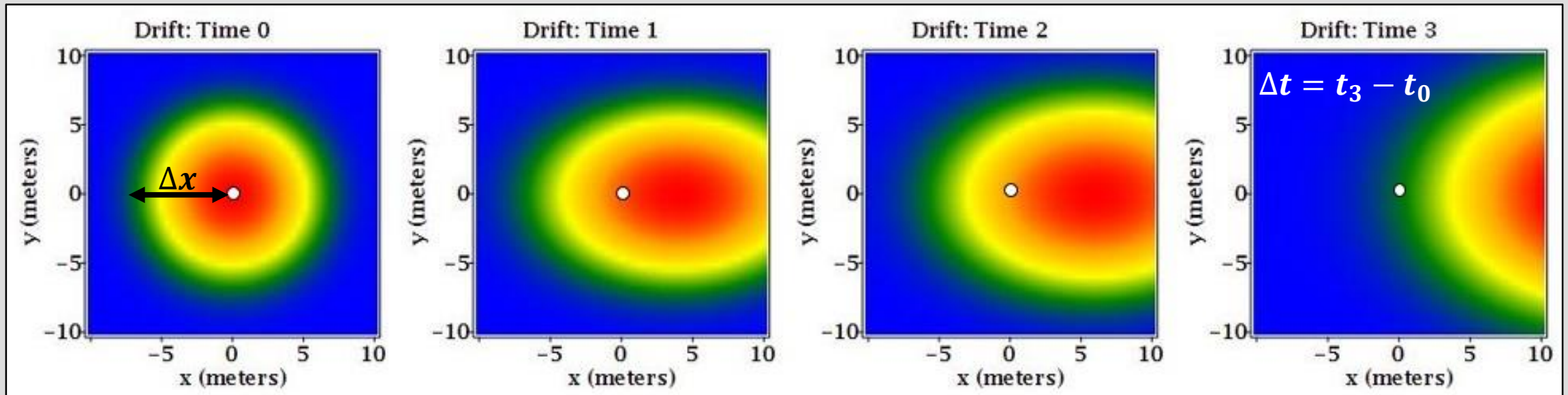
Paradis et. al., (2019) _Groundwater_ **(In Review)**

DRIFT-PHASE BREAKTHROUGH CURVES (MODEL)

■ **Drift phase**: mean travel time ($\bar{t}$) should be inversely proportional to velocity ($\vec{v}$)

■ $\vec{v} = \dfrac{\bar{x}}{\bar{t}}$

Model Breakthrough Curves

C/Co vs Time (hours)

— v = 0.5 m/d ····· v = 1 m/d — — v = 2 m/d — · — v = 4 m/d

DRIFT-PHASE BREAKTHROUGH CURVES (MODEL)

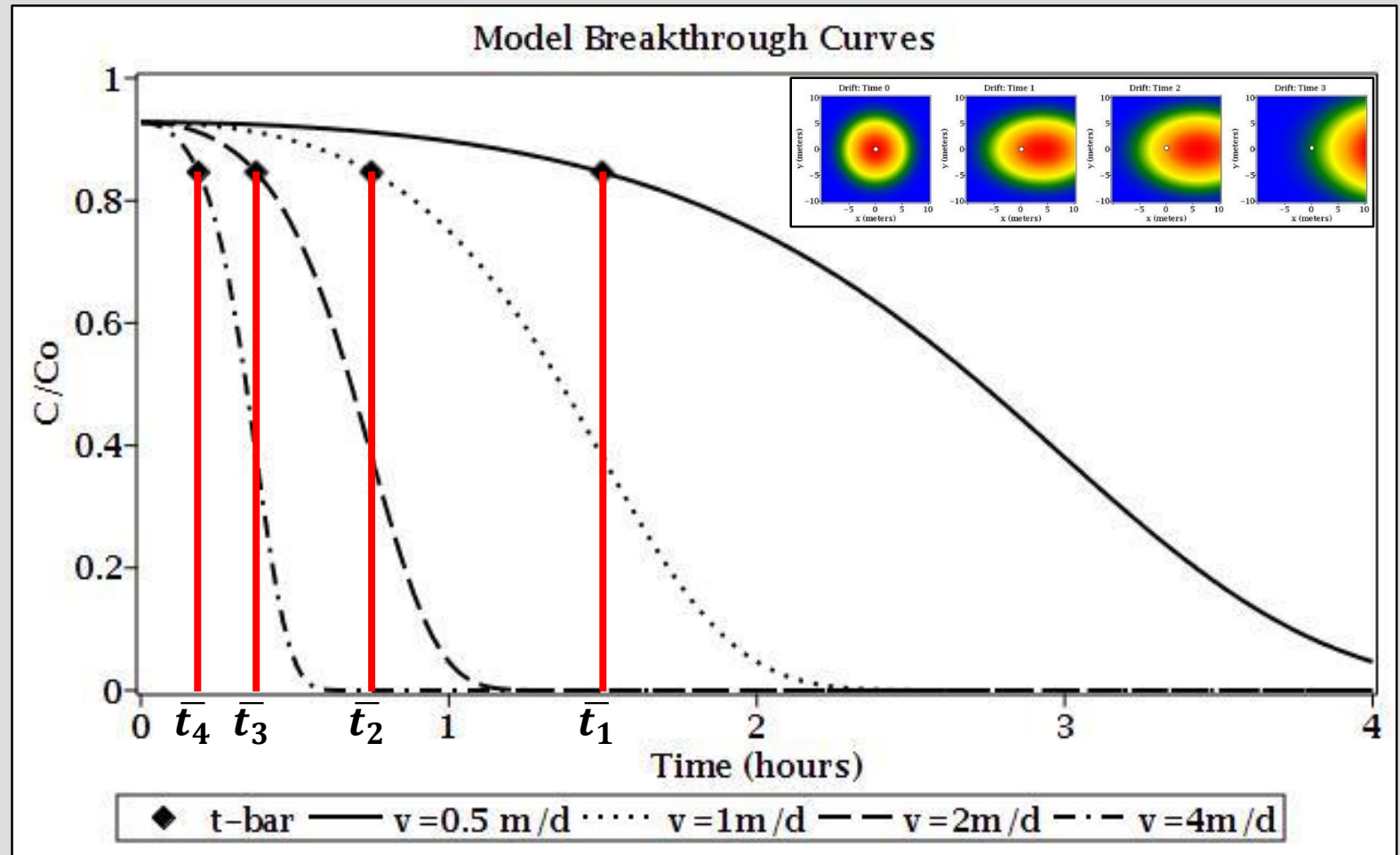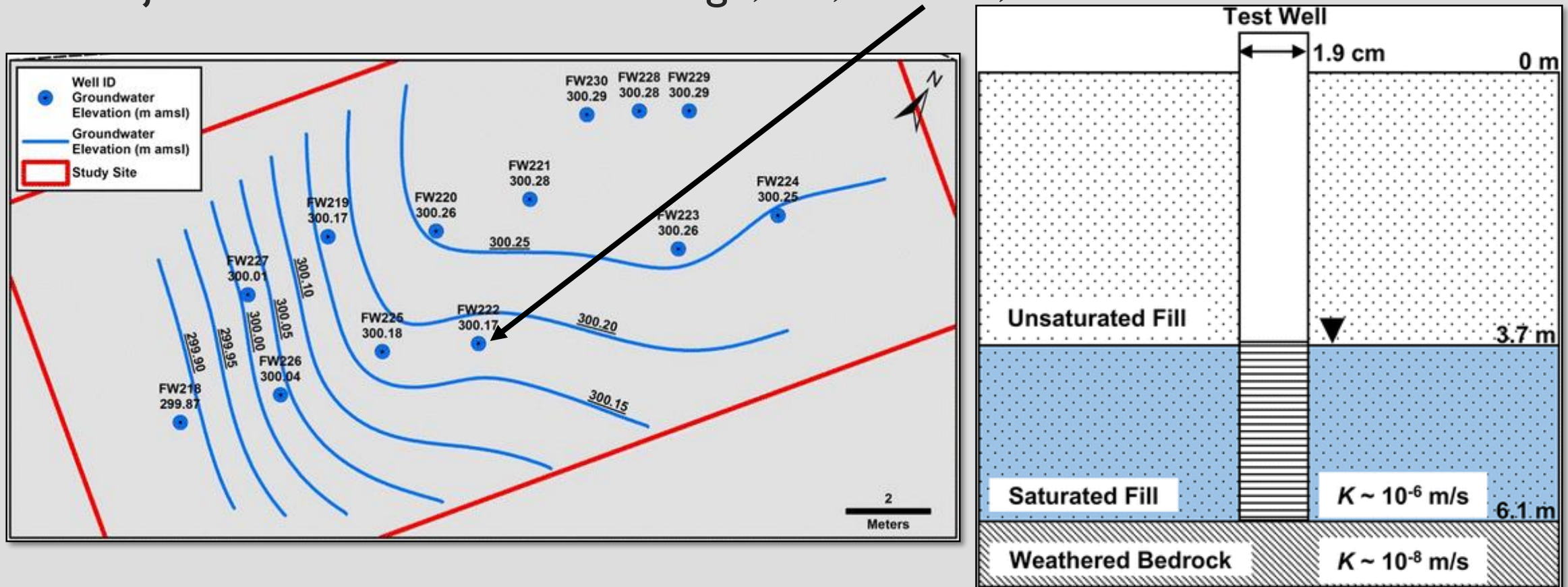■ **Drift phase**: mean travel time ($\bar{t}$) should be inversely proportional to velocity ($\vec{v}$)

■ $\vec{v} = \dfrac{\bar{x}}{\bar{t}}$

Model Breakthrough Curves

24
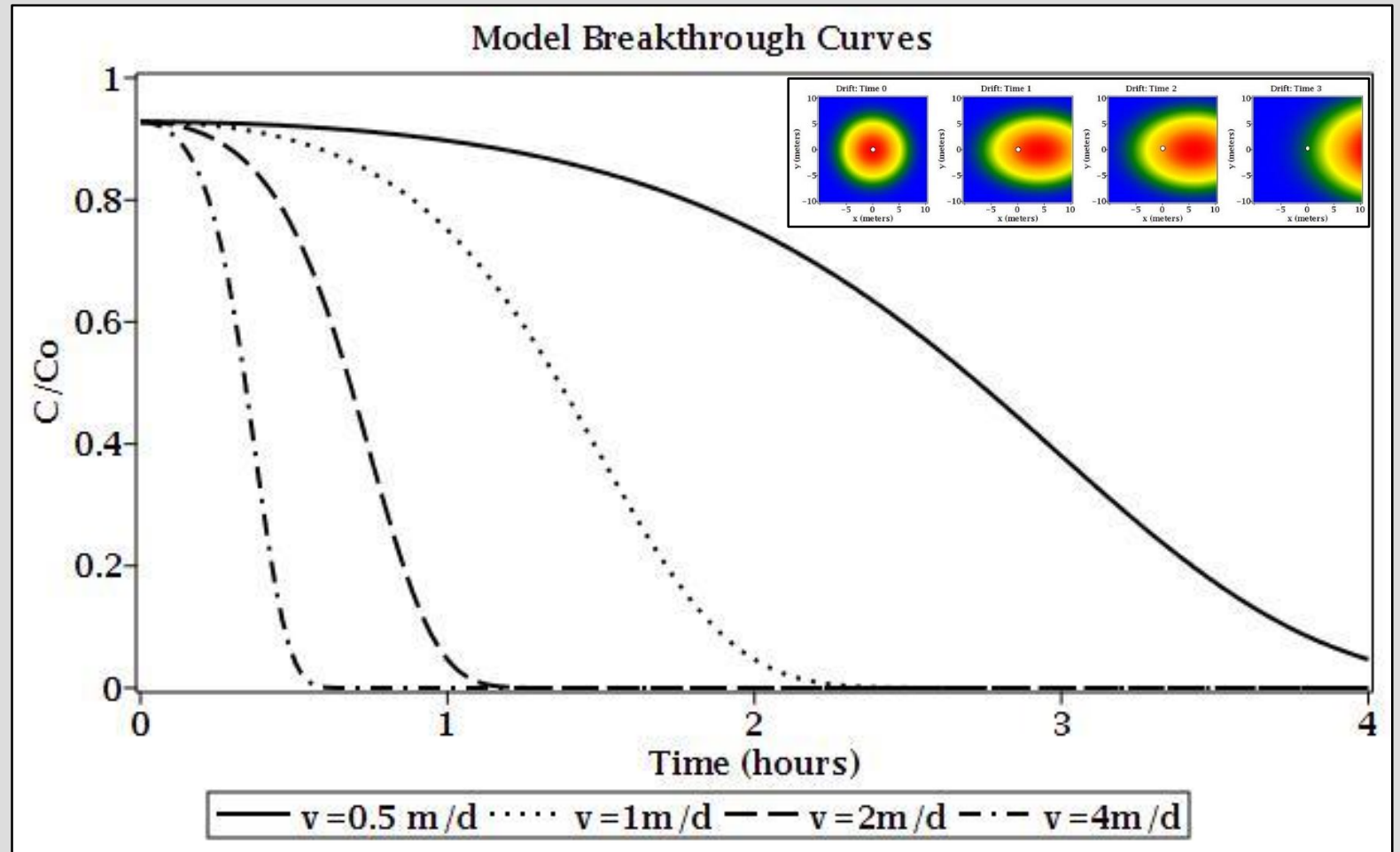
SINGLE-WELL INJECTION-DRIFT (FIELD TEST)

- 6 injection-drift tests at Oak Ridge, TN, FW222, Br^- tracer


Paradis et. al., (2019) _Groundwater_ **(In Review)**

SINGLE-WELL INJECTION-DRIFT (MODEL & DATA)

- Data & model yield nearly identical mean travel times ($\bar{t}$)
- Model fits velocity ($\vec{v}$)
- Velocity ($\vec{v}$) agrees with previous multi-well natural-gradient tests

$\vec{v} \approx 1m/day$

$\vec{v} \approx 3m/day$

Paradis et. al., (2019) *Groundwater* **(In Review)**
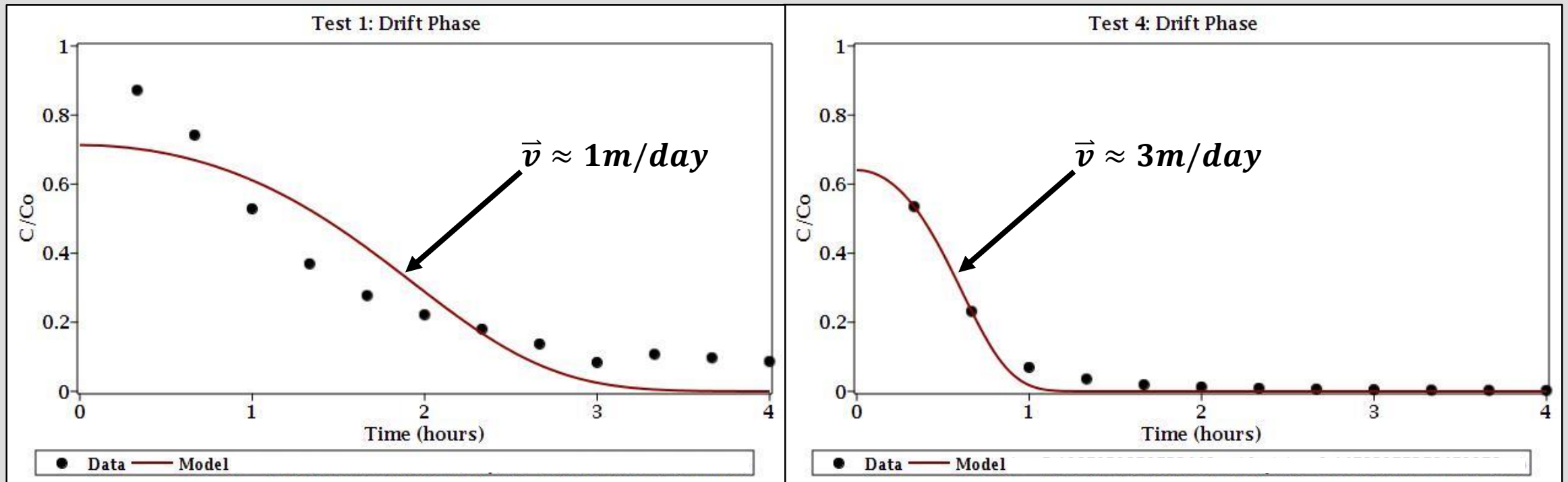
SINGLE-WELL INJECTION-DRIFT (MODEL & DATA)

■ Data & model nearly identical mean travel times ($\bar{t}$)

■ Characterize temporal variations in $\vec{v}$, slow and fast $\vec{v}$

Paradis et. al., (2019) _Groundwater_ **(In Review)**
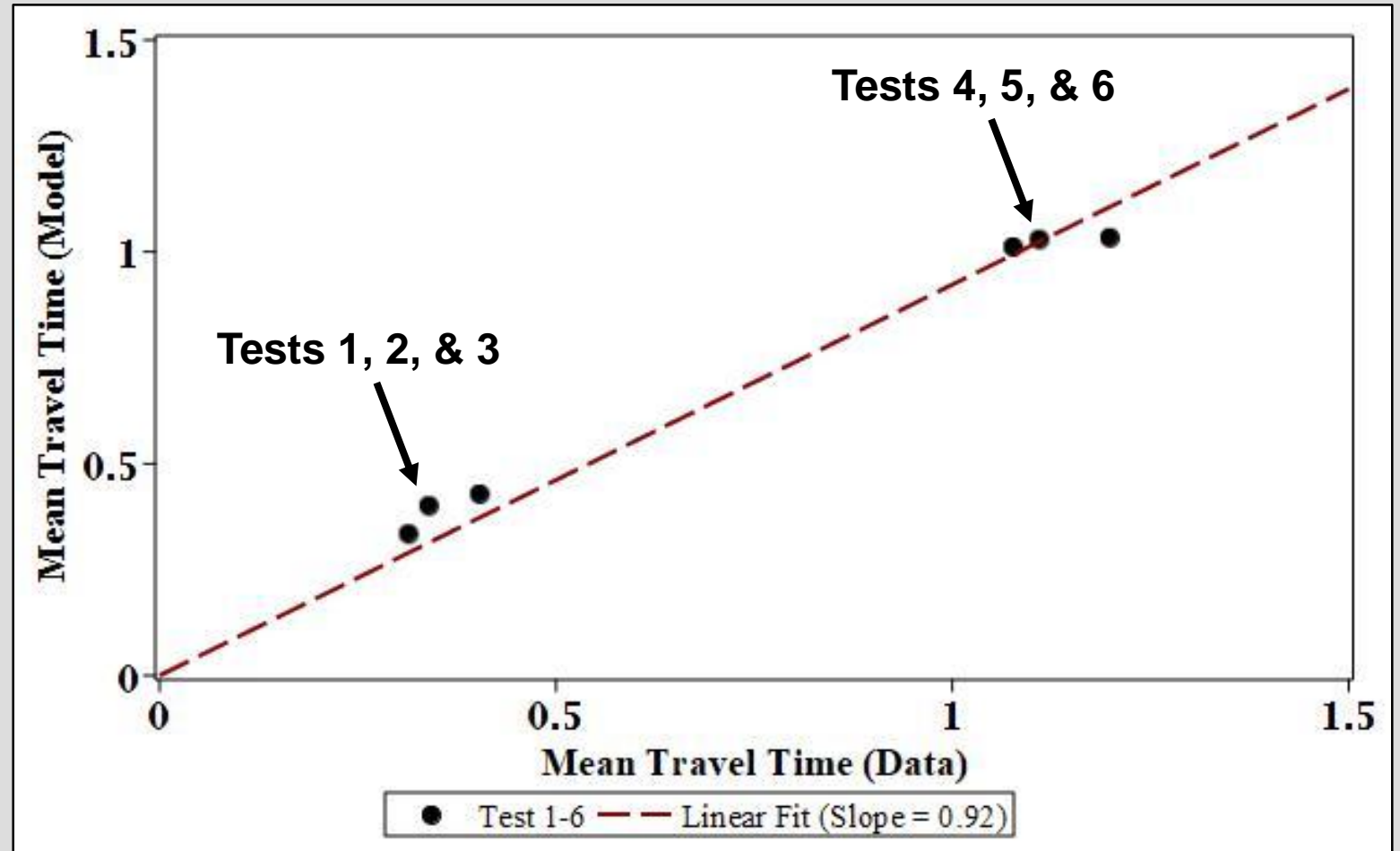
NEW CHARACTERIZATION METHOD: FUTURE RESEARCH QUESTION

- **How accurate can new method characterize the TRUE groundwater velocity ($\vec{v}$) ?**

- True groundwater velocity ($\vec{v}$) in the field is unknown…

- Grad. project 1: test new method physical model, know ($\vec{v}$)

- Grad. project 2: test new method numerical model, know ($\vec{v}$)

NEW CHARACTERIZATION METHOD: FUTURE PHYSICAL MODELS

- Flow in (Q_{in}) equal to flow out (Q_{out})
- $\vec{v} = \dfrac{Q}{An_e}$
- Start simple: clean sand, confined aquifer, homogeneous, isotropic

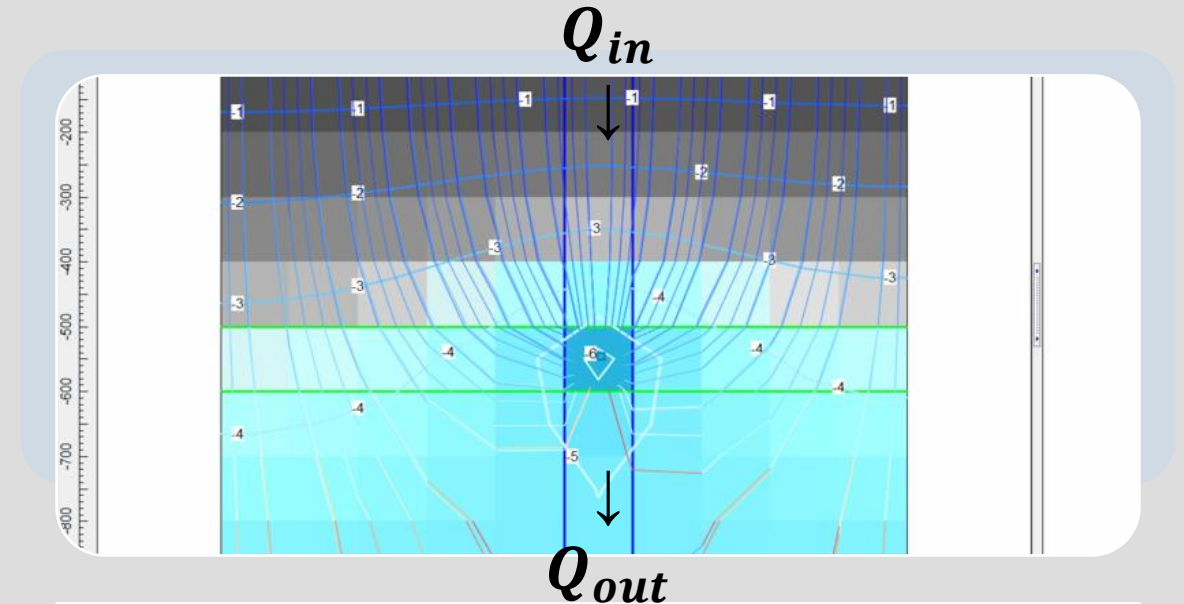$Q_{in} \rightarrow$ $\rightarrow Q_{out}$

Physical Models

1-D Column

2-D Ant Farm

3-D Fish Tank

NEW CHARACTERIZATION METHOD: FUTURE NUMERICAL MODELS

- Flow in (Q_{in}) equal to flow out (Q_{out})

- $\vec{v} = \dfrac{Q}{An_e}$

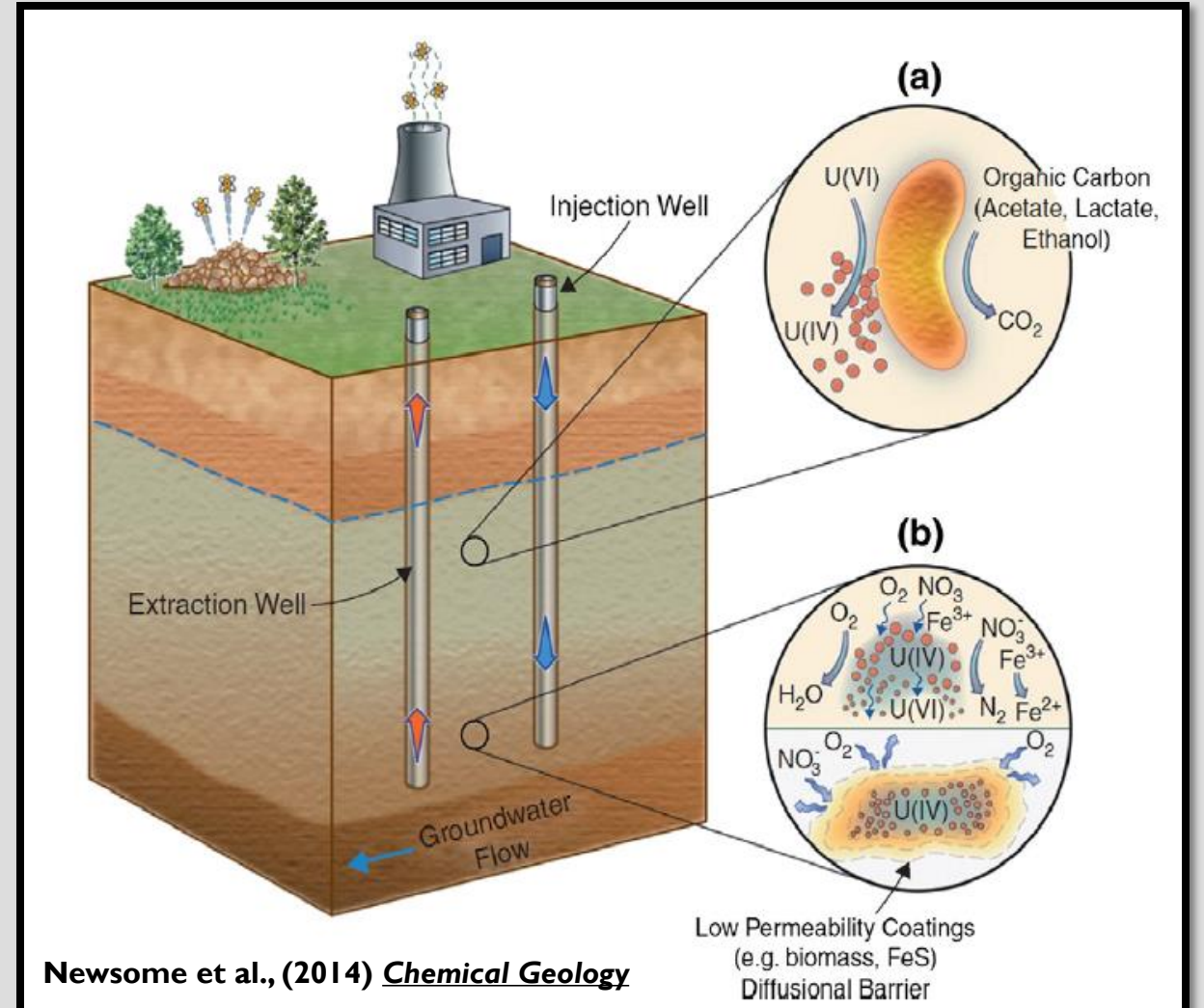- Easily increase complexity: unconfined, heterogeneous, anisotropic

Q_{in}

Q_{out}

Numerical Model
MODFLOW code
MODPATH code
ModelMuse GUI

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URANIUM BIOGEOCHEMISTRY

- U^{4+} (uraninite) immobile
- U^{6+} (uranyl) mobile

- Immobilization/Reduction
- $U^{6+} + EtOH \rightarrow U^{4+} + CO_2$

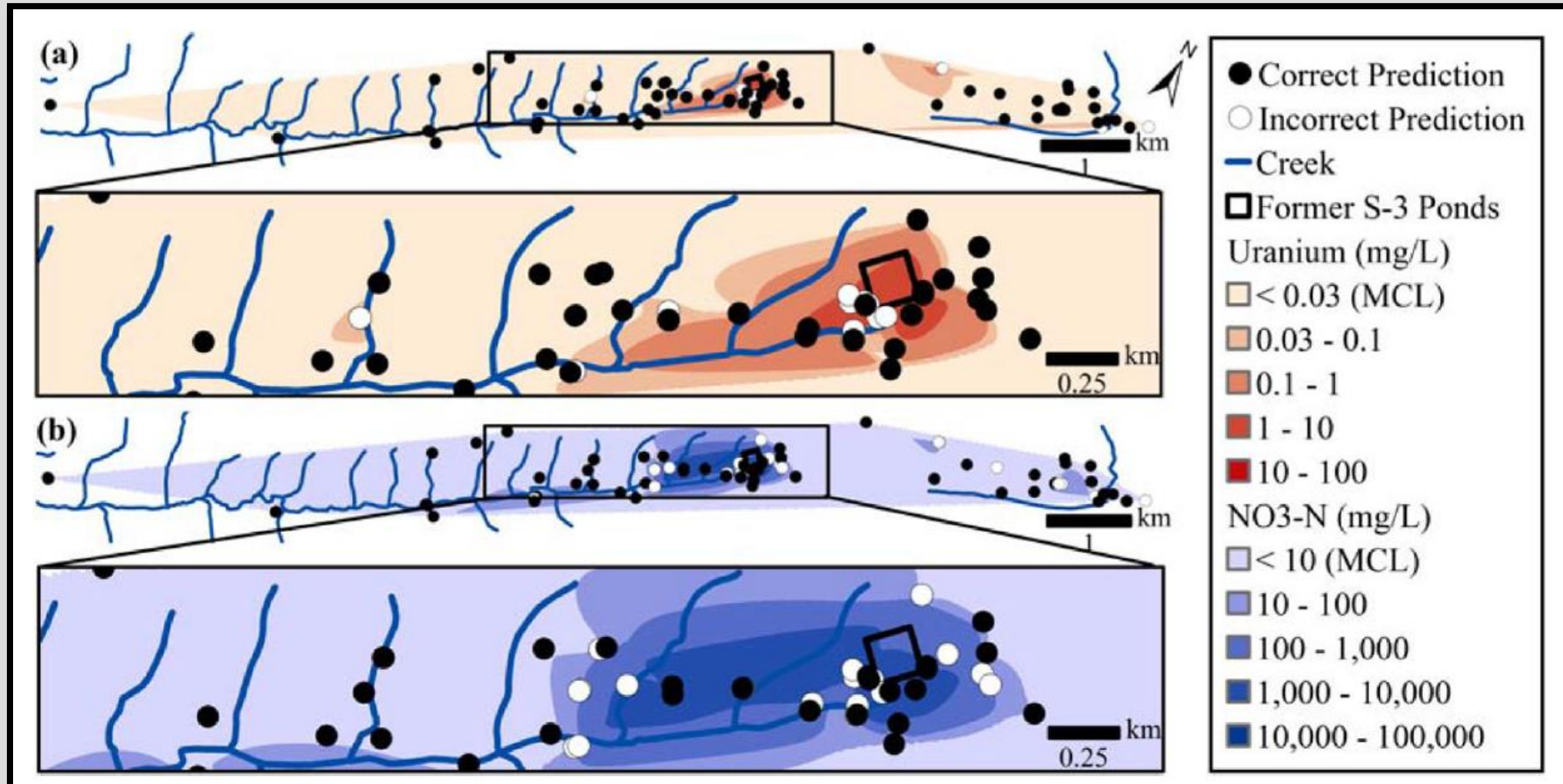- Mobilization/Oxidation
- $NO_3^- + U^{4+} \rightarrow U^{6+} + N_2$

(a) U(VI) — Organic Carbon (Acetate, Lactate, Ethanol); U(IV), CO_2

(b) O_2 NO_3 Fe^{3+} NO_3^- Fe^{3+} U(IV) U(VI) H_2O N_2 Fe^{2+} NO_3^- O_2 U(IV) Low Permeability Coatings (e.g. biomass, FeS) Diffusional Barrier

Injection Well

Extraction Well

Groundwater Flow

Newsome et al., (2014) *Chemical Geology*

URANIUM THERMODYNAMICS

- Thermo predicts oxidation of reduced sulfur-bearing species by NO_3^- preferential to uraninite ($UO_{2(im)}$)

- $UO_{2(im)} + NO_3^- \approx -405 \; kJ$

- $S^0 + NO_3^- \approx -430 \; kJ$

- $FeS + NO_3^- \approx -459 \; kJ$

- $FeS_2 + NO_3^- \approx -423 \; kJ$

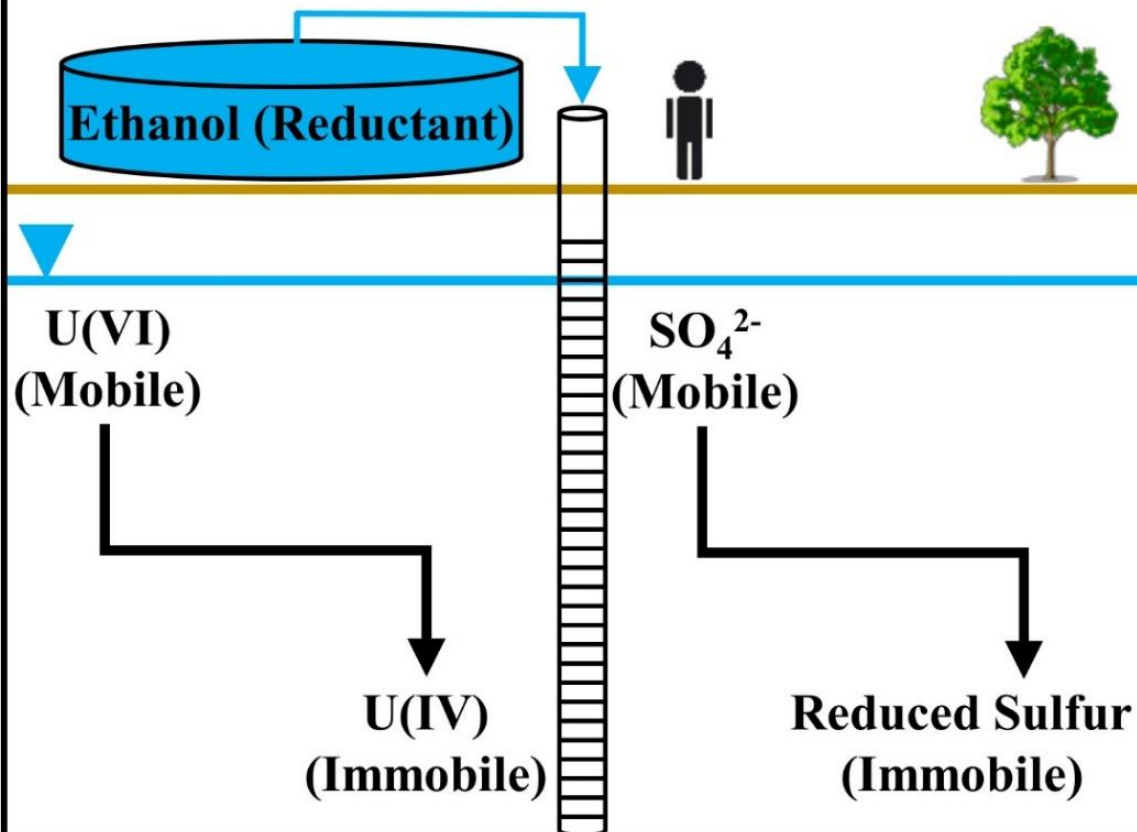- $MnS + NO_3^- \approx -479 \; kJ$

RESEARCH QUESTION #2

- **Can promoting sulfur-reducing conditions limit uranium (U^{4+}) re-mobilization/re-oxidation in presence of NO_3^-?**
- Field experiment at uranium- and nitrate-contaminated site
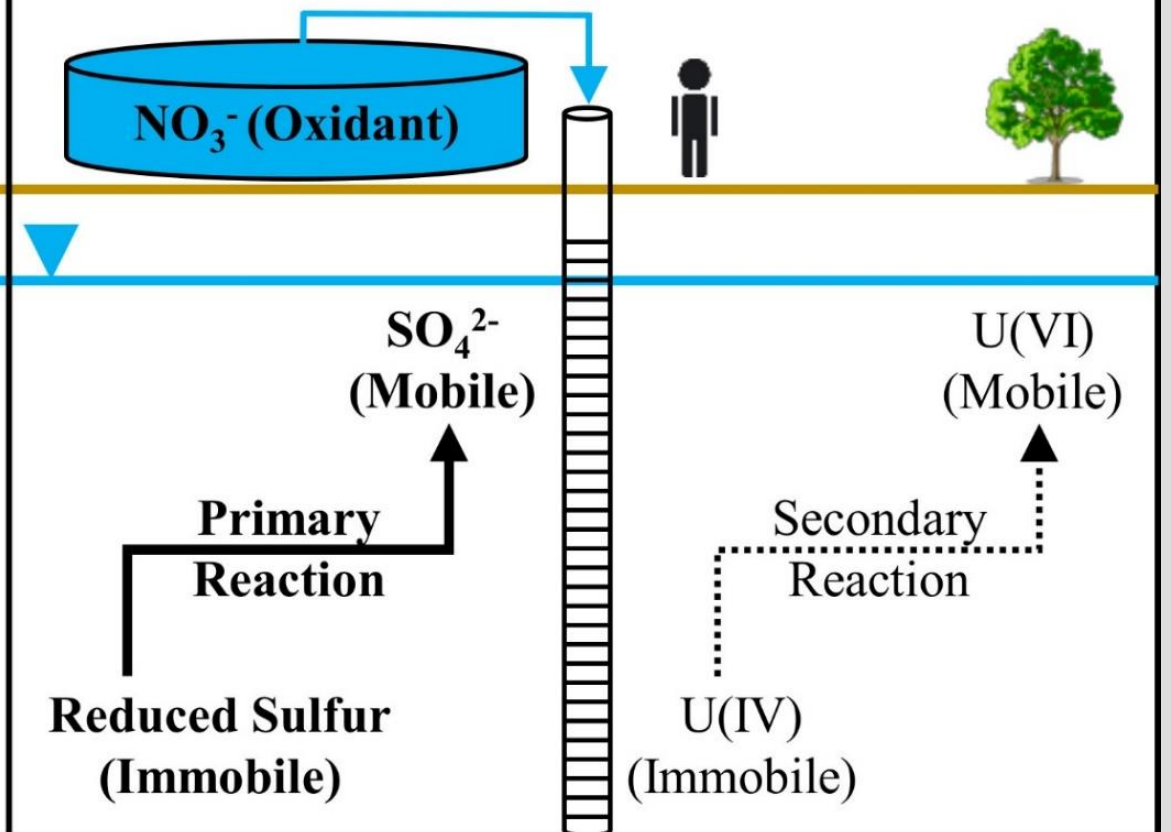
OAK RIDGE, TN (U^{6+} & NO_3^-)

Smith et. al., (2015) *MBio*

FIELD EXPERIMENT

First Reduce/Immobilize Uranium & Sulfate

Then Test Oxidation/Mobilization of Uranium by NO_3^-

Ethanol (Reductant)

NO_3^- (Oxidant)

U(VI) (Mobile)

SO_4^{2-} (Mobile)

SO_4^{2-} (Mobile)

U(VI) (Mobile)

Primary Reaction

Secondary Reaction

U(IV) (Immobile)

Reduced Sulfur (Immobile)

Reduced Sulfur (Immobile)

U(IV) (Immobile)

URANIUM & SULFATE DATA

- **Extraction-phase breakthrough curves post- NO_3^- injection**
- NO_3^- **decrease**
- NO_2^- **increase**
- SO_4^{2-} **increase**
- U^{6+} **stable**

Paradis et. al., (2016) *Journal of Contaminant Hydrology*
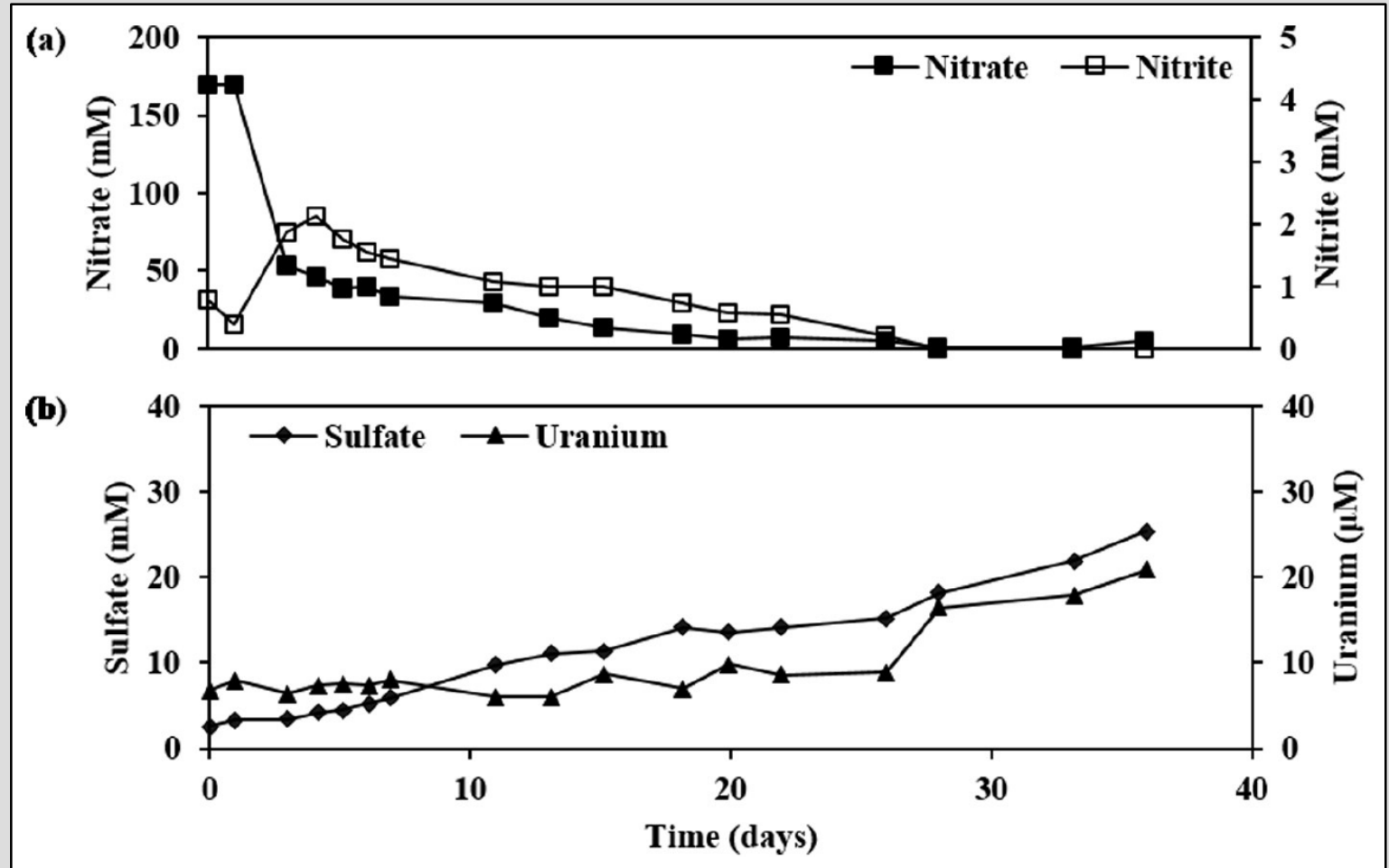
URANIUM & SULFATE DATA

- **≈10x more sulfate extracted relative to bromide**

- **Uranium and bromide extracted nearly equal**

- <u>**Improved method for sustained immobilization of uranium**</u>

Treatment ID	Well	Amendments	U(VI)	SO_4^{2-}
Control	FW224	30 mM EtOH, 20 mM SO_4^{2-}	0.2	0.5
Cluster 1	FW219	120 mM NO_3^-	1.0	14.4
	FW220		1.5	8.6
	FW225		1.5	13.0

Paradis et. al., (2016) *Journal of Contaminant Hydrology*

IMPROVED REMEDIATION METHOD: FUTURE RESEARCH QUESTION

- **What is mineralogy of uranium-bearing and sulfur-bearing species pre- and post-ethanol & -nitrate injections?**

- Mineralogy in the field is unknown…

- Grad project 3: characterize mineralogy and geochemistry to better understand mechanisms of uranium/sulfur re-oxidation

IMPROVED REMEDIATION METHOD: FUTURE PHYSICAL MODELS

- Pack columns w/seds from Oak Ridge, TN site

- $UO_{2(m)}^{2+} + EtOH \rightarrow UO_{2(im)} + CO_2$

- $NO_3^- + FeS_{2(im)} \rightarrow SO_{4(m)}^{2-} + N_2$

- $NO_3^- + UO_{2(im)} \rightarrow UO_{2(m)}^{2+} + N_2$

- Sequence sacrifice columns, pre- and post- injections for mineralogy & geochemistry

T_1 = polluted groundwater
T_2 = sterilized polluted groundwater with sodium azide

Peristaltic pump

Column R_1 Column R_2 Column R_3 Column R_4 Column R_5
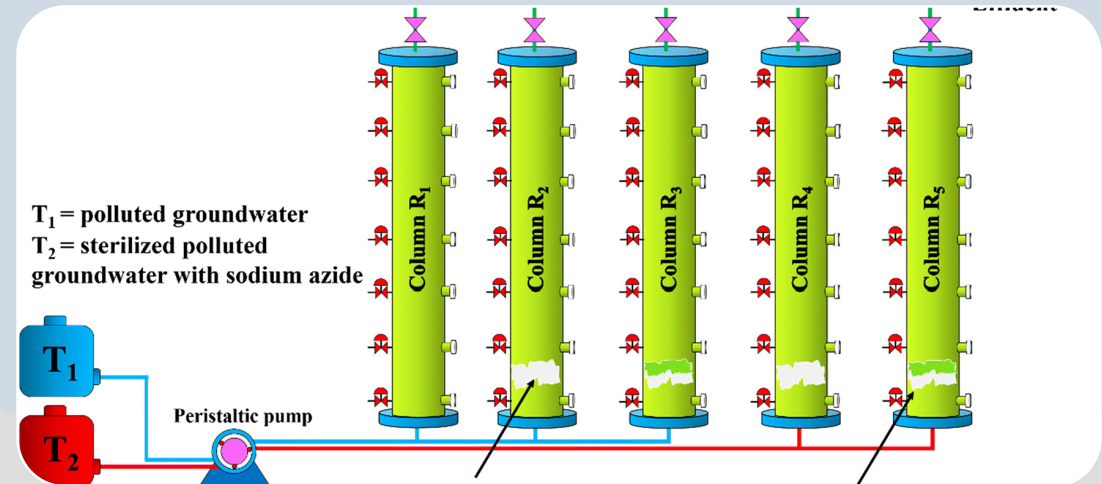
Physical Models
1-D Columns
XRF (elemental abundance)
(Q)XRD (mineral & quantity)

NITRATE BIOGEOCHEMISTRY

■ Molybdenum (Mo) **KEY** for nitrate reductase

■ Mo not always bioavailable, ppt w/Fe/Al

Ge et al., (2018) *Environmental Microbiology*

Ge et al., (2018) *Environmental Microbiology*
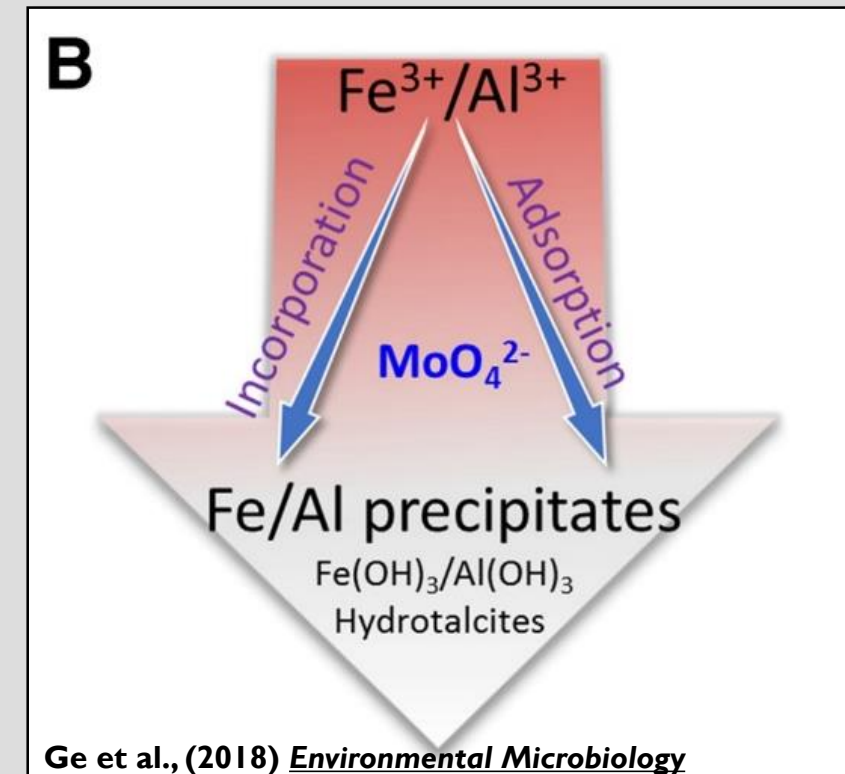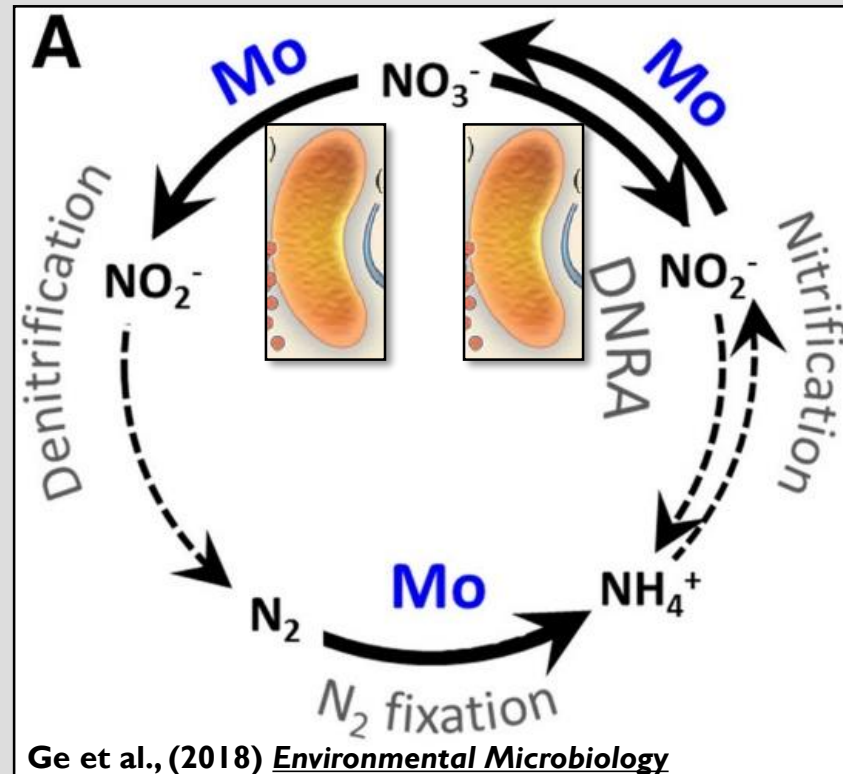
RESEARCH QUESTION #3

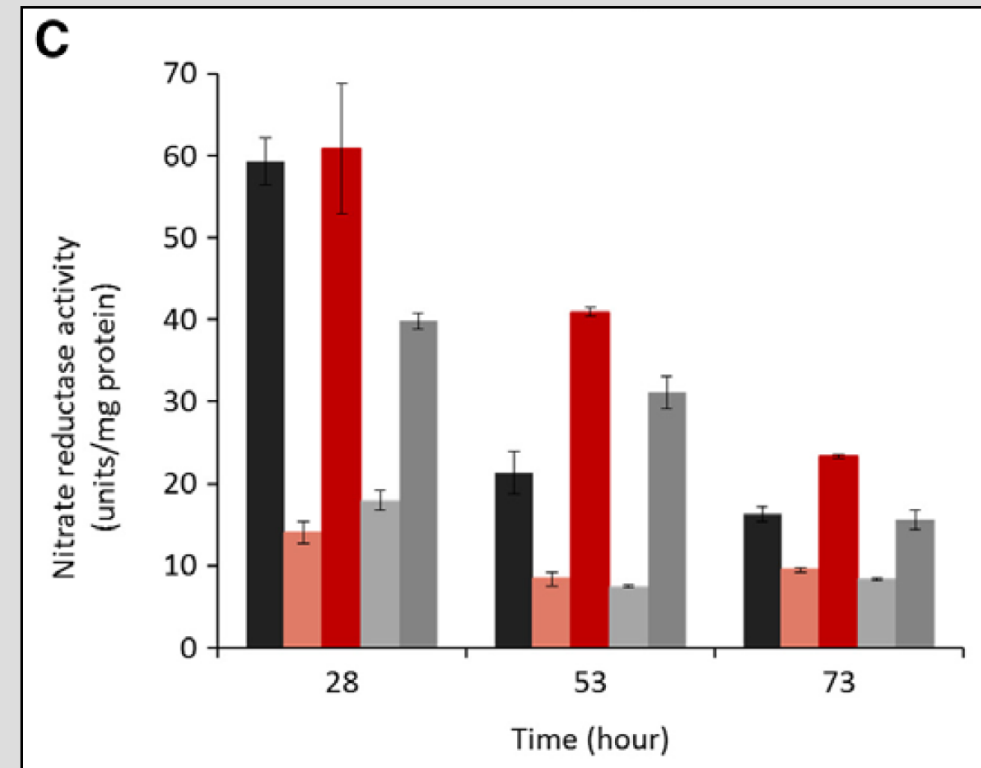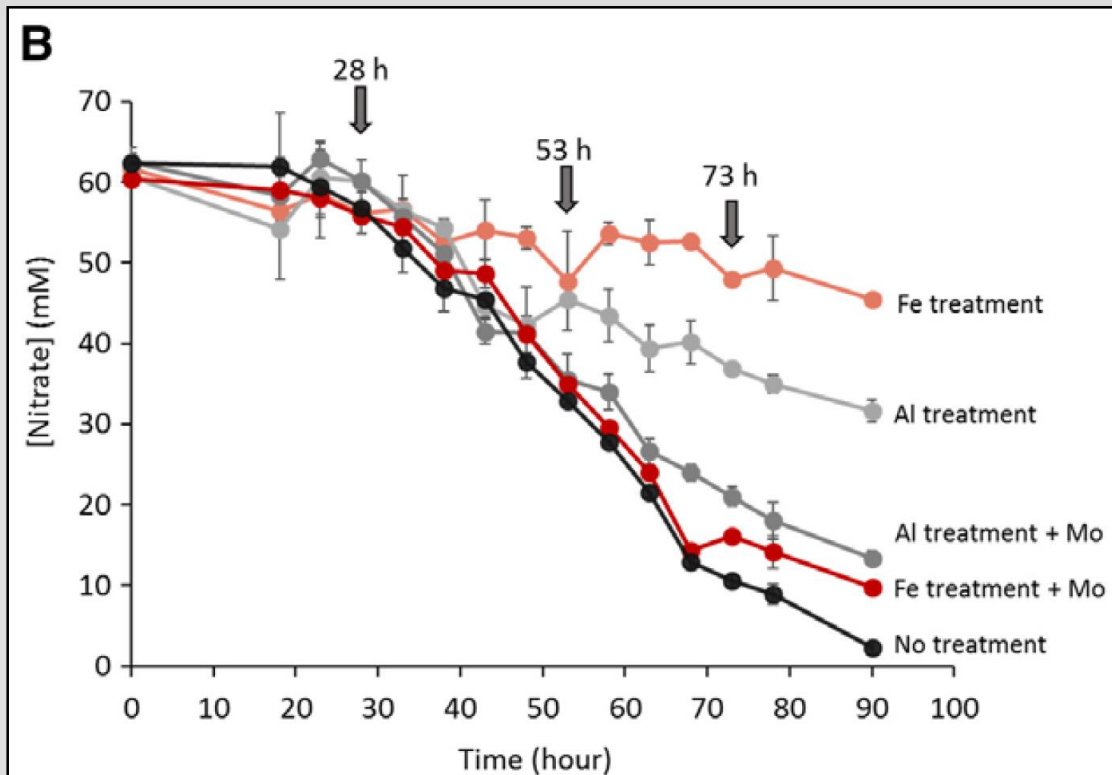- **Can lack of bio-available Mo contribute to persistent NO_3^-?**

Smith et. al., (2015) *MBio*
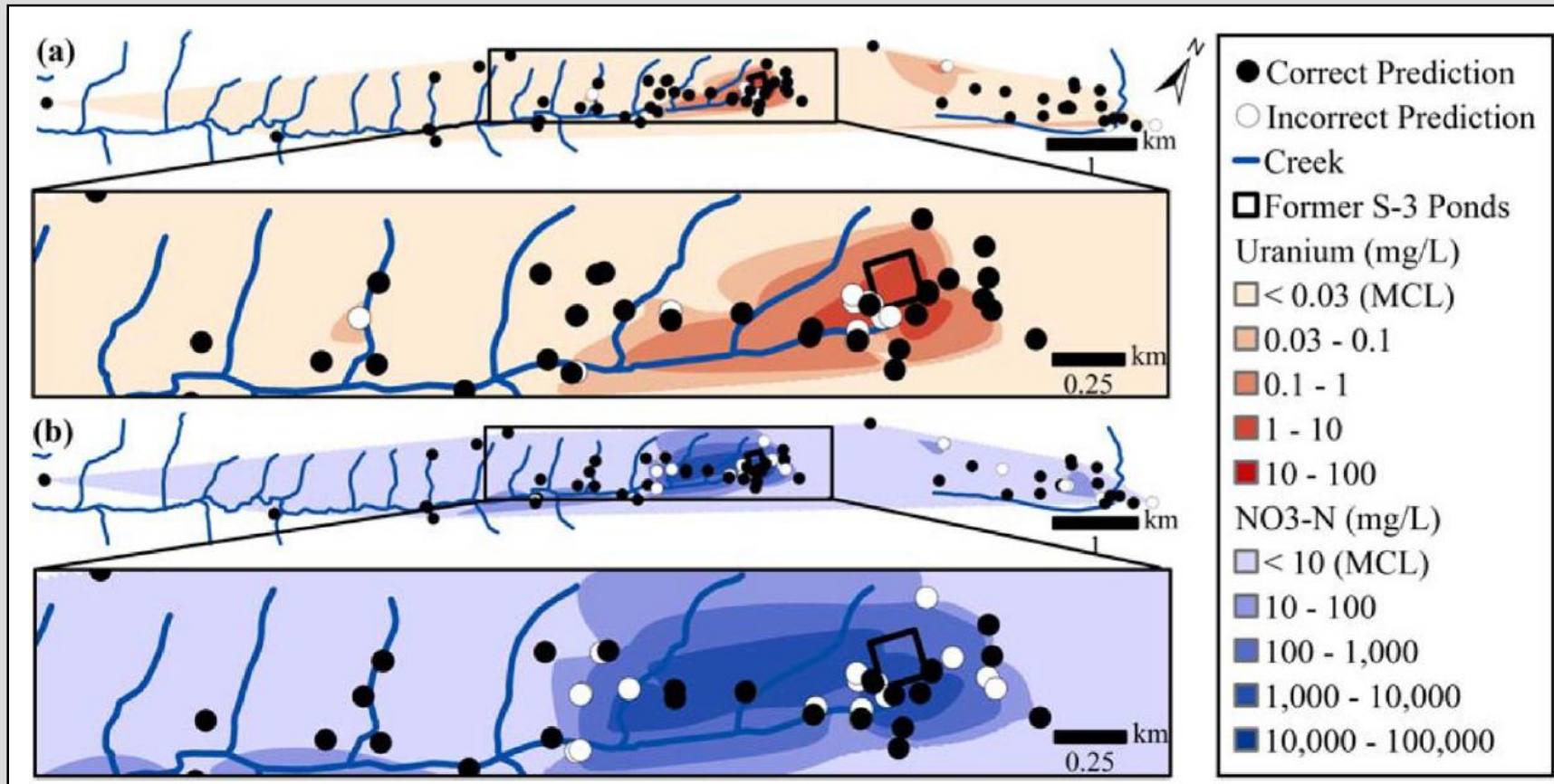
FIELD DATA SUGGESTS YES

■ **Soluble Mo decrease w/increase in Al and Fe and low pH**
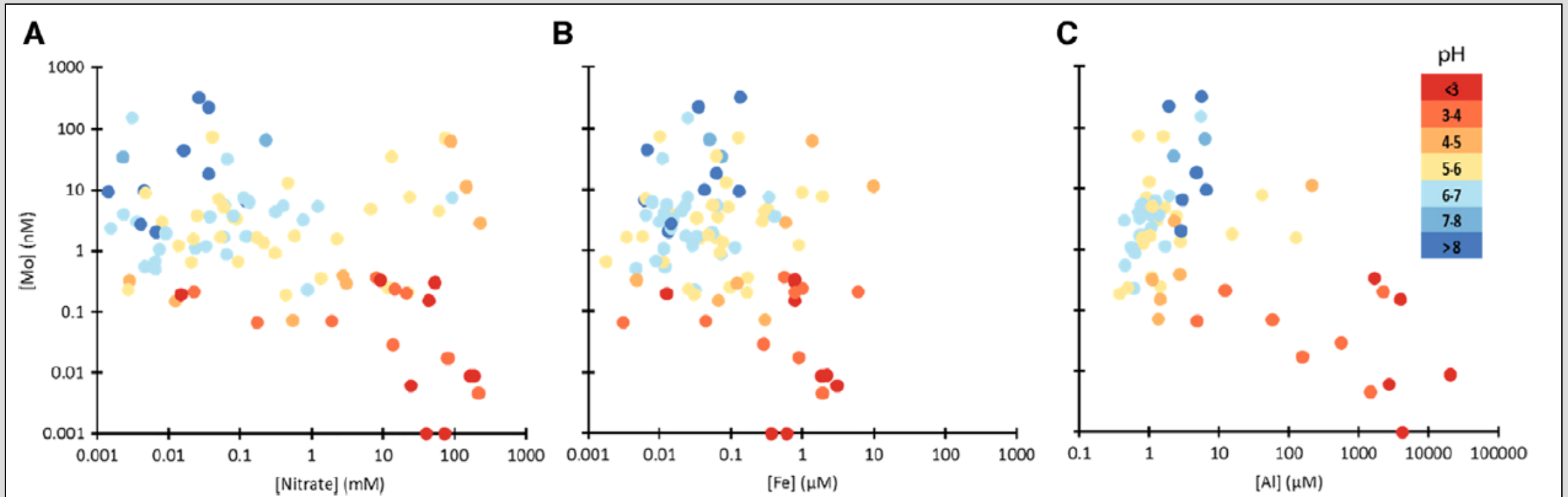
LAB EXPERIMENT DATA

- **Test w/Oak Ridge isolate, growth media, synthetic groundwater**
- **Data demonstrates lack of bio-Mo contributes to persistent NO$_3^-$**

Ge et. al., (2018) *Environmental Microbiology*

Mo-LIMITED NITRATE BIO-REDUCTION: FUTURE RESEARCH QUESTIONS

- **Are results from Ge et al., (2018) repeatable during conditions that better represent the field?**

- Ge et al., (2018) used microbial isolate, growth media, synthetic groundwater

- Graduate student project 4: repeat Ge et al., (2018) experiments with microbial community and native sediments and groundwater
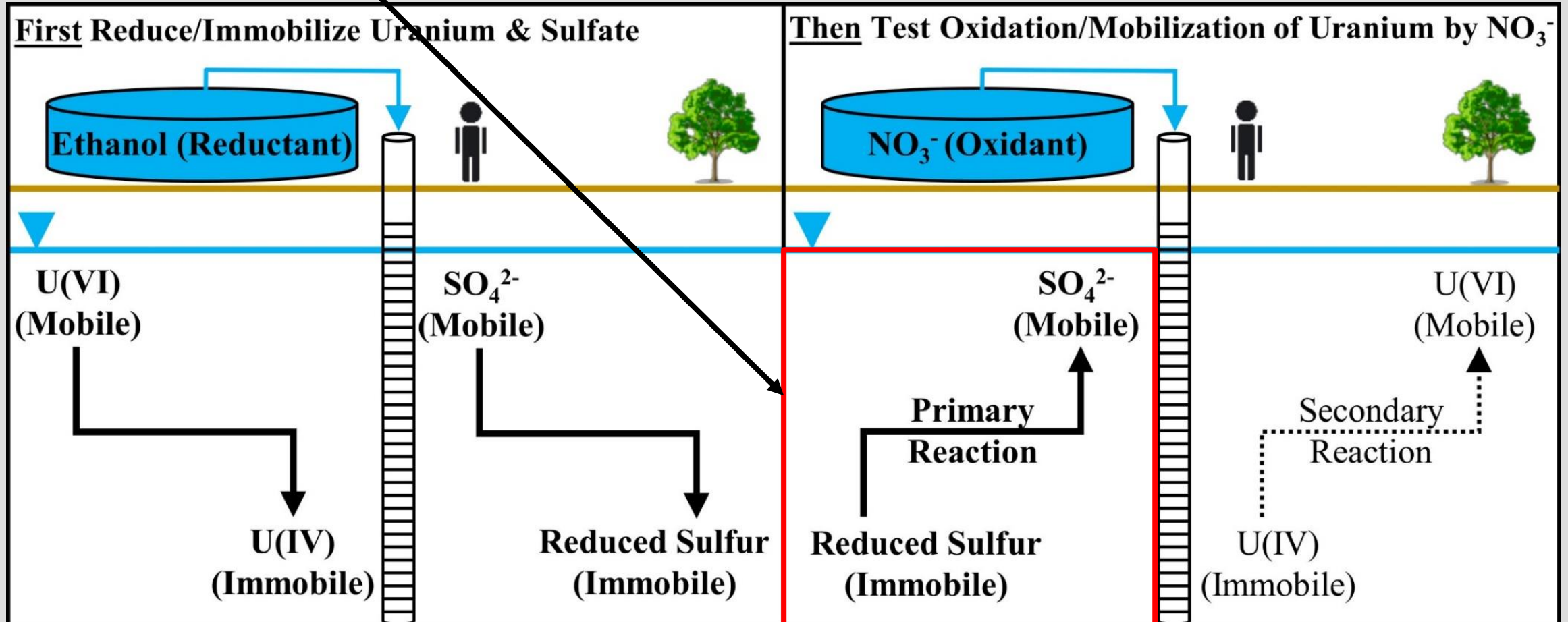
OBJECTIVES: BROAD (SUMMARY)

- Improve existing and develop new methods of in-situ characterization and remediation

- Incorporate microbiology to better understand and predict contaminant transport

NEW METHOD CHARACTERIZE $\vec{v}$

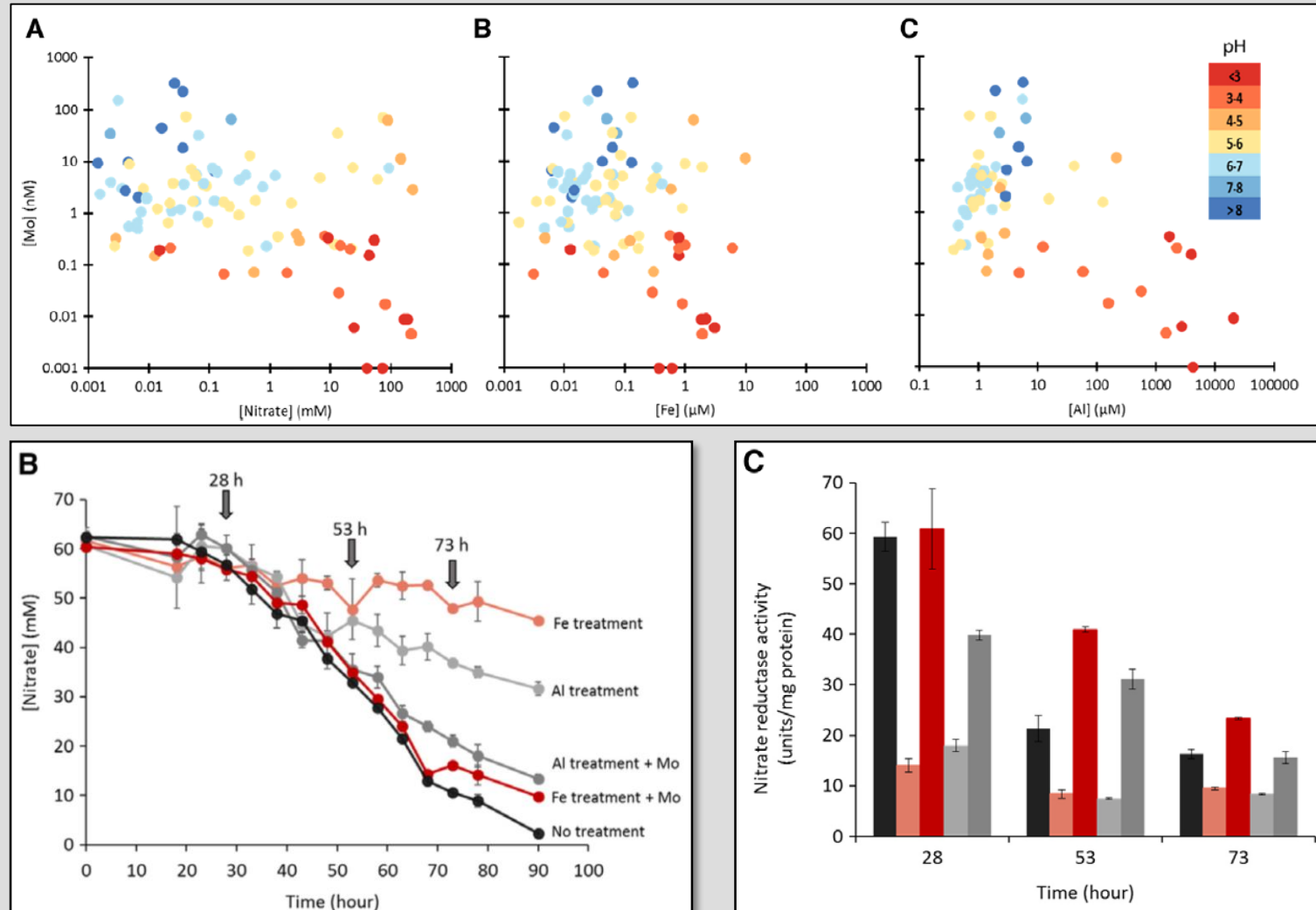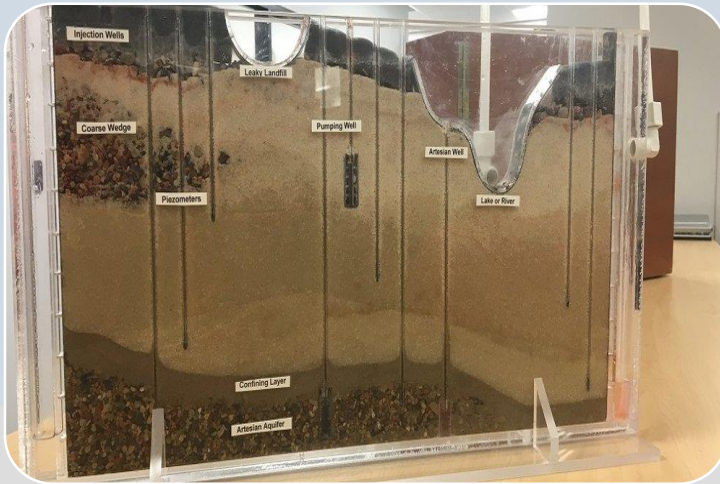Slow $\vec{v}$

Fast $\vec{v}$
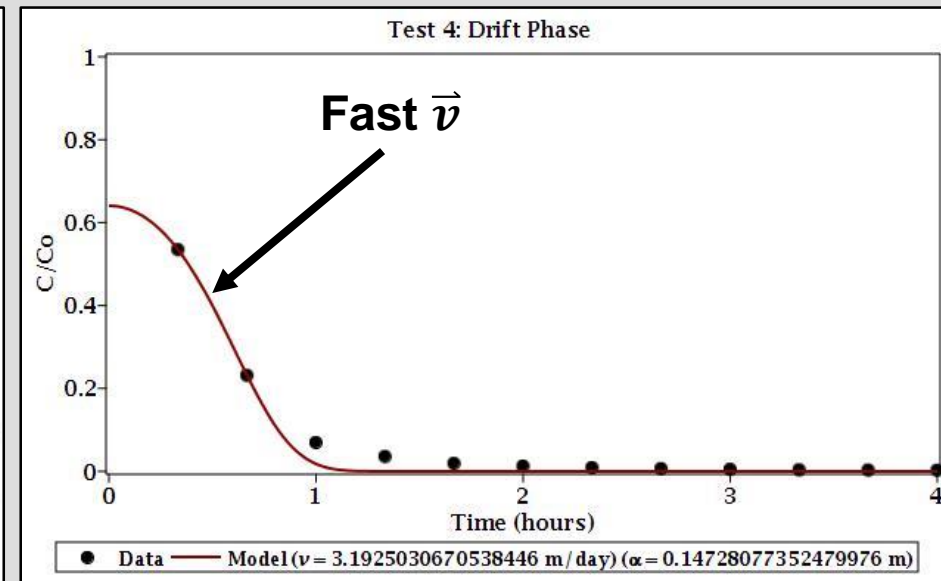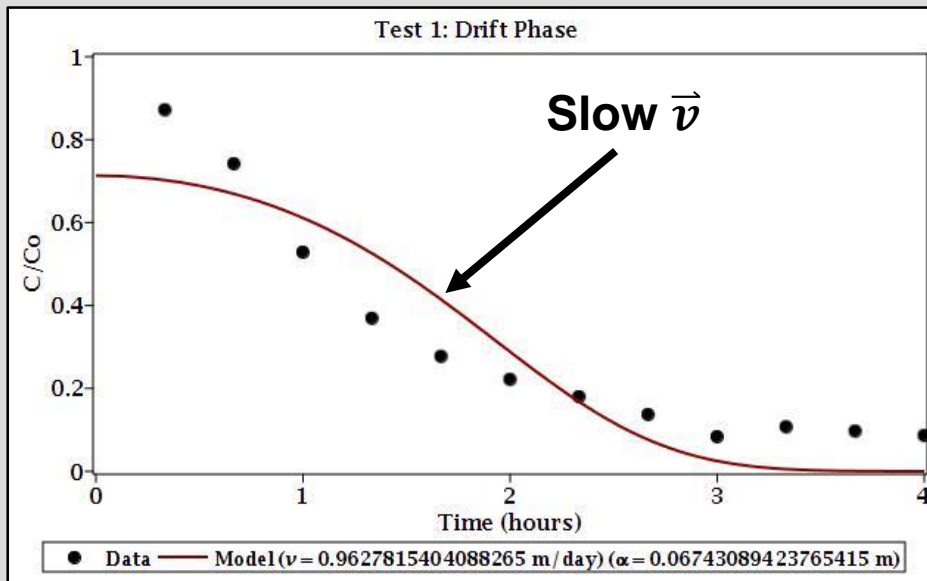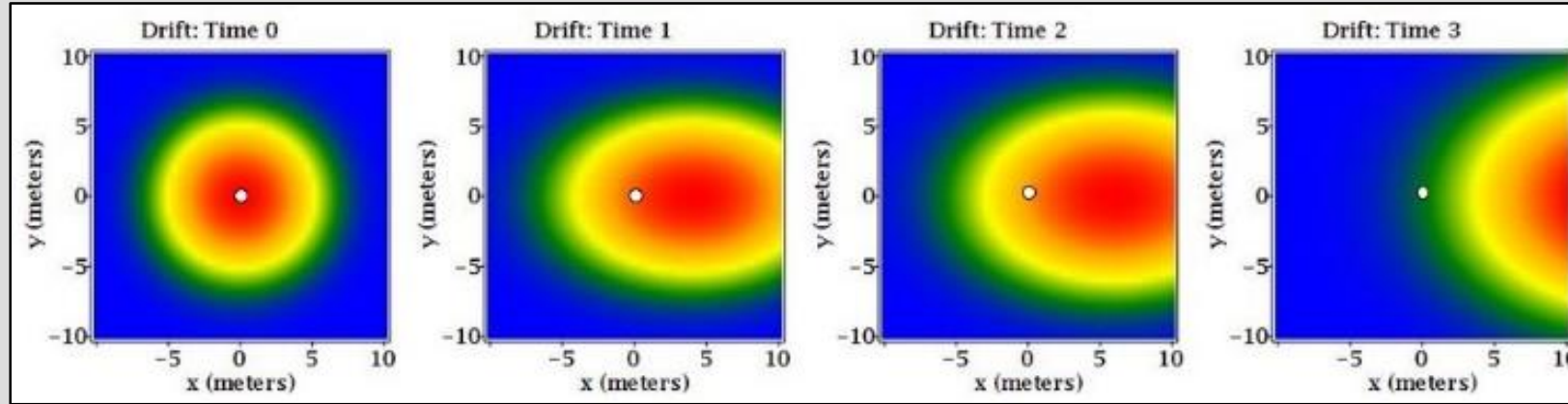
IMPROVED METHOD IMMOBILIZE U^{6+}

OBJECTIVES: BROAD (SUMMARY)

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- Incorporate microbiology to better understand and predict contaminant transport

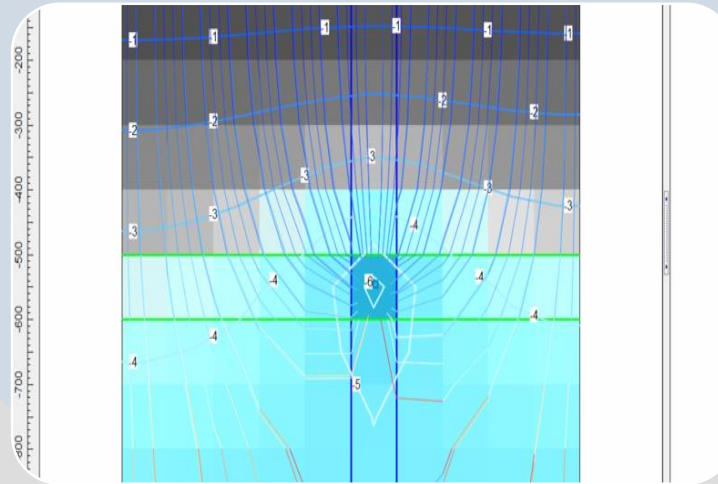# DEMONSTRATE GEO-LIMITATION ON BIO-REDUCTION OF NITRATE

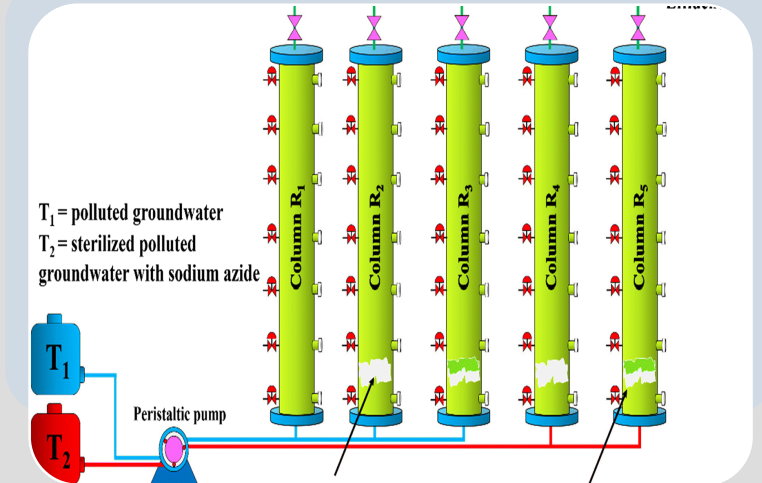# FUTURE RESEARCH: GRADUATE STUDENTS

Physical Models

1-D Column

2-D Ant Farm

3-D Fish Tank

Numerical Model

MODFLOW code

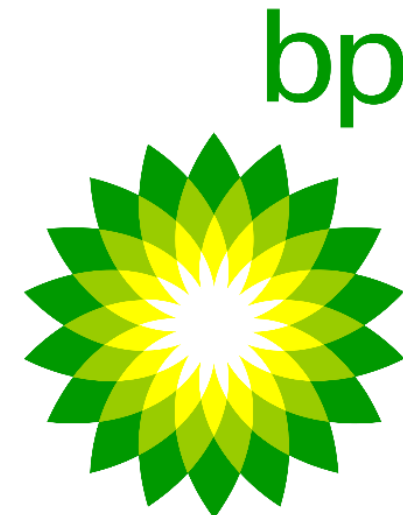MODPATH code

ModelMuse GUI

Physical Models

1-D Columns

XRF (elemental abundance)

(Q)XRD (mineral & quantity)

ACKNOWLEDGEMENTS: SPONSORS

QUESTIONS & COMMENTS?