

Training Students in Simulation & Risk Assessment for Carbon Sequestration

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Department of Civil and Environmental Engineering



U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the
Infrastructure for CO₂ Storage
August 21-23, 2012

Presentation Outline

- Benefits to Program
- Project Overview: Goals, objectives, tasks
- Accomplishments
- Technical Status and Findings
- Summary: Lessons Learned & Future Work
- Bibliography

Benefit to the Program

Program goals being addressed.

- Develop technologies that will support industries' ability to predict CO₂ storage capacity in geologic formations to within ±30 percent.

From the RFP: "... provide training opportunities for graduate and undergraduate students that will provide the human capital and skills required for implementing and deploying CCS technologies. Training can be accomplished through fundamental research Fundamental research is needed to advance science in: simulation and risk assessment; verification, and accounting;and integrity for long-term CO₂ storage and capture.

Benefit to the Program

Our project has two goals: training and research.

Training: 2 M.S. and one 1 PhD student will receive degrees and can continue in the arena of carbon sequestration. 1 post-doctoral student has received technical and project-management training. A university course has been developed and delivered twice. The training enables advance professionals to enter the GCS field.

Research: (a) developing simulation methodologies to better understand and predict leakage of CO₂ from the injection zone, and impact of leakage on aquifers, (b) experiments to understand impacts of CO₂ leakage on aquifer water quality. *The research should enhance public confidence in sequestration, and enable better prediction of storage efficiencies.*

Project Overview: Goals and Objectives

The primary objectives of the project are to *train students* and *advance the science* in two critical areas of risk assessment:

- (1) multi-process, multi-scale characterization and model simulation of the risks associated with leakage into overlying aquifers;
- (2) pore-scale geochemical processes in CO₂ sequestration...including mineral reactivity and multiphase fluid reactions, needed to assess the likelihood of an successful sequestration effort.

Project Overview: Goals and Objectives

Success criteria:

- MS students complete thesis and receive graduate degrees
- PhD student completes required exams, dissertation, and receives PhD degree.
- Post-doctoral researcher achieves career position
- Experiments and simulations are completed.
- Peer-reviewed journal articles are submitted/accepted (goal: 1 per MS student and 3 per PhD student, and 1 additional for the per team)

Project Overview:

Goals and Objectives : Tasks

Task	Percent Complete	FY 2010				FY 2011				FY 2012				FY 2013
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13
<i>Task 1: Project Management Plan and Reporting</i>	90%													
1.1 Project Management Plan (PMP)	100%													
1.2 Planning and Reporting	90%		A	B	C		D				E			
<i>Task 2: Quantifying risk associated with leakage of CO₂ into overlying aquifers</i>														
2.1 Lit review on CO ₂ leakage and impacts on aquifer water quality	100%													
2.2 Lit review on toxicity of CO ₂ leakage byproducts.	100%					G								
2.3 Identification of scenarios	90%				F		J	K						
2.4 Risk assessment modeling	90%											N		P
<i>Task 3: Laboratory experiments and associated modeling to elucidate pore-scale geochemical processes associated with carbon injection, storage and sequestration</i>														
3.1 Detailed sample characterization	60%					H								
3.2 Laboratory experiments	60%							L						
3.3 Reanalysis of samples from experiments	25%													
3.4 Geochemical modeling	10%													O
<i>Task 4: Seminar taught for course credit on risk-assessment associated with CO₂ sequestration</i>														
4.1 Develop course syllabus	100%						I							
4.2 Develop course materials	100%													
4.3 Deliver Course	100%							M						

Accomplishments to Date

- Alexis Sitchler (PhD Penn State) has received training as a project manager for this project, and recently agreed to a tenure-track faculty position in the Geology & Geological engineering Dept at CSM. She will continue a career in GCS research.
- Erica Siirilla (B.S. Univ. Colorado) completed M.S. Thesis and degree (grad date Dec 2010), and entered PhD program at CSM. Expected to graduate in May 2013
- Hannah Menke (B.S. Columbia Univ) completed her M.S. thesis, defends tomorrow at 9:30 am. Will continue on to a PhD program in carbon sequestration at Imperial College (London).
- Katy Kirsch started an M.S. Thesis (Hydrology) in May.

Accomplishments to Date

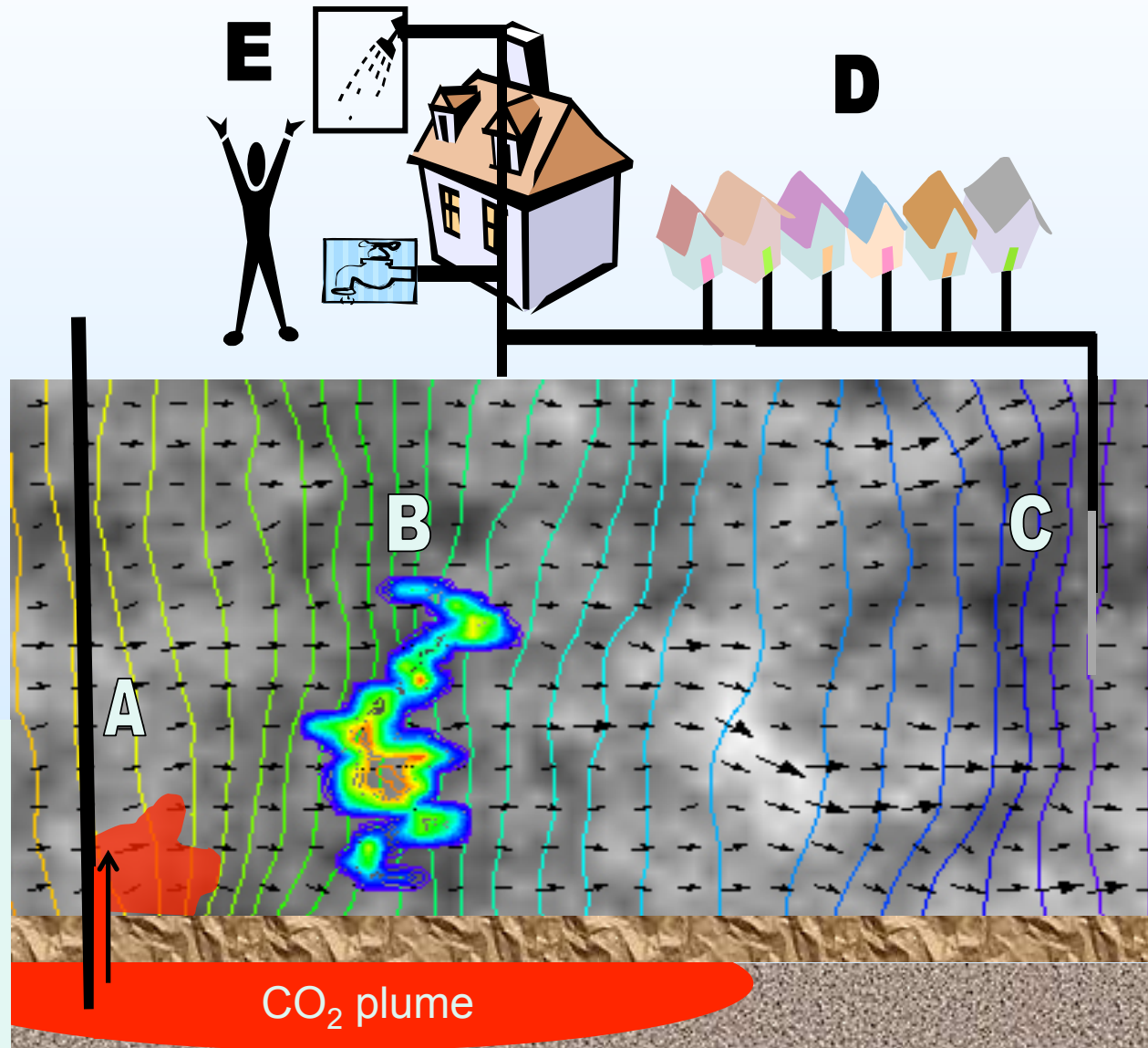
- Developed and delivered (twice) a graduate-level course (ESGN/GEGN 598) on carbon sequestration, focusing on fundamental applied concepts and papers from the literature. More than 35 graduate students received training via course.
- Post-Doc (Navarre-Sitchler) and two PhD students (Siirilla, Wunsch) participated in teaching carbon sequestration and/or risk in ESGN/GEGN 598 and ESGN/GEGN 581 (risk assessment).
- 2 M.S. Theses completed (Siirilla and Menke)
- 3 peer-reviewed papers completed.
- Risk assessment methodology created.
- Experimental protocol developed, experiments underway

Technical Status

Because this is a training grant, we have arranged this section by student:

- Erica Siirilla
- Hanna Menke
- Katie Kirsch

Siirilla 1. Development of a Quantitative Human Health Risk Framework for CO₂ Leakage



A: CO₂ leakage and dissolution of metals

B: Heterogeneous flow and transport of metals

C: Possible capture in one or more down-gradient wells

D: Water delivery system to many different households

E: Household exposure and health risk via multiple pathways to varying individuals



A quantitative methodology to assess the risks to human health from CO₂ leakage into groundwater

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Monte Carlo
Human health risk
Joint Uncertainty and Variability

ABSTRACT

Leakage of CO₂ and associated gases into overlying aquifers as a result of geologic carbon capture and sequestration may have adverse impacts on aquifer drinking-water quality. Gas or aqueous-phase leakage may occur due to transport via faults and fractures, through faulty well bores, or through leaky confining materials. Contaminants of concern include aqueous salts and dissolved solids, gaseous or aqueous-phase organic contaminants, and acidic gas or aqueous-phase fluids that can liberate metals from aquifer minerals. Here we present a quantitative risk assessment framework to predict potential human health risk from CO₂ leakage into drinking water aquifers. This framework incorporates the potential release of CO₂ into the drinking water aquifer; mobilization of metals due to a decrease in pH; transport of these metals down gradient to municipal receptors; distributions of contaminated groundwater to multiple households; and exposure and health risk to individuals using this water for household purposes. Additionally, this framework is stochastic, incorporates detailed variations in geological and geostatistical parameters and discriminates between uncertain and variable parameters using a two-stage, or nested, Monte Carlo approach. This approach is demonstrated using example simulations with hypothetical, yet realistic, aquifer characteristics and leakage scenarios. These example simulations show a greater risk for arsenic than for lead for both cancer and non-cancer endpoints, an unexpected finding. Higher background groundwater gradients also yield higher risk. The overall risk and the associated uncertainty are sensitive to the extent of aquifer stratification and the degree of local-scale dispersion. These results all highlight the importance of hydrologic modeling in risk assessment. A linear relationship between carcinogenic and noncarcinogenic risk was found for arsenic and suggests action levels for carcinogenic risk will be exceeded in exposure situations before noncarcinogenic action levels, a reflection of the ratio of cancer and non-cancer toxicity values. Finally, implications for ranking aquifer vulnerability due to geologic configuration, aquifer mineralogy, and leakage scenarios are discussed.

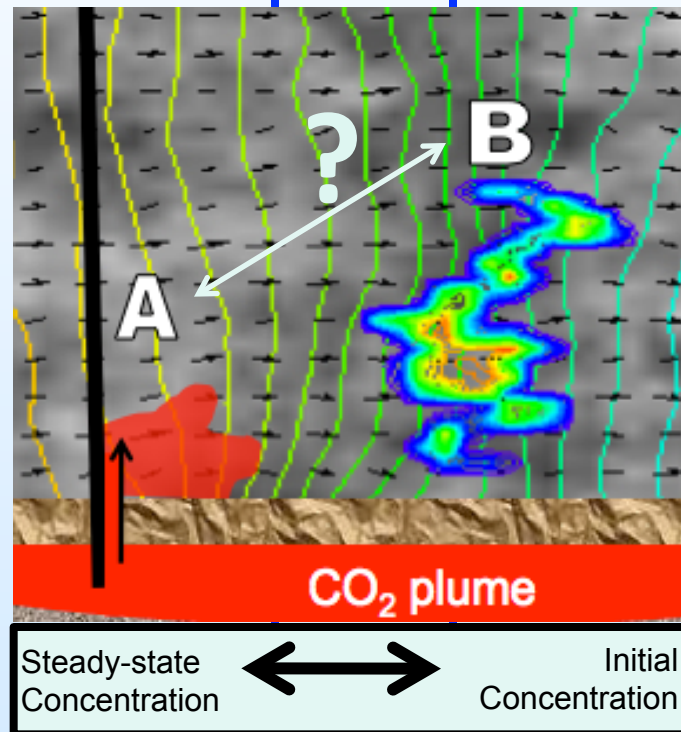
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Drawing Connections Between Geochemical Reactions and Aquifer Transport at Different Scales

(A) At the leakage source:

- Multi-component, nonlinear geochemical reactions and fluid transport
- Run until a steady-state metal concentration and pH are achieved

Answers questions such as, “*How does mineralogy composition affect the risk?*”



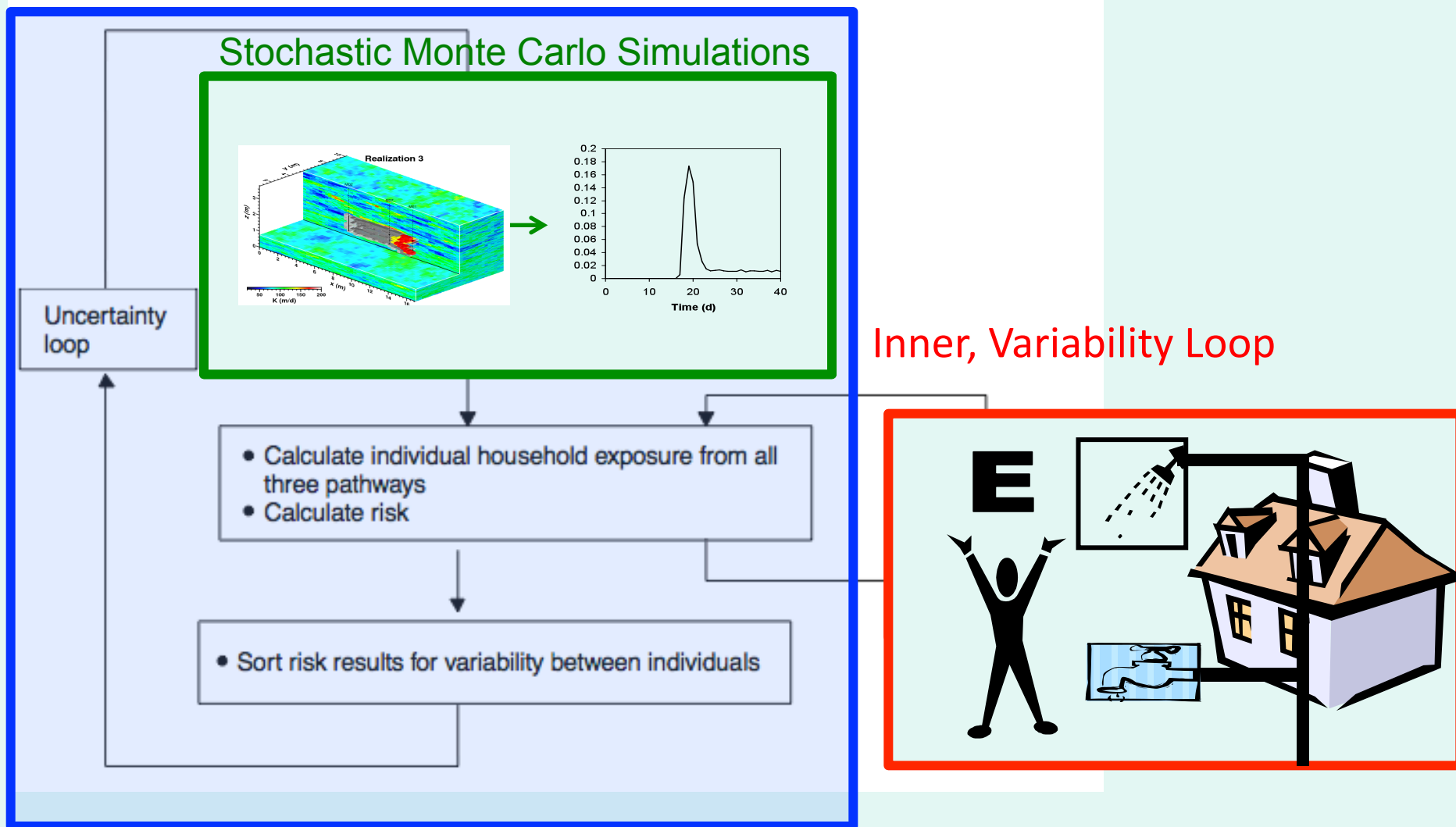
(B) Far-field aquifer:

- Steady-state concentration from (A) used as initial metal concentration
- Contaminant plume modeled with a particle-tracking technique
- Linear reactions

Answers questions such as, “*How does aquifer stratification affect the risk?*”

Includes a Robust, Probabilistic Treatment of Risk: The Nested Monte Carlo Approach

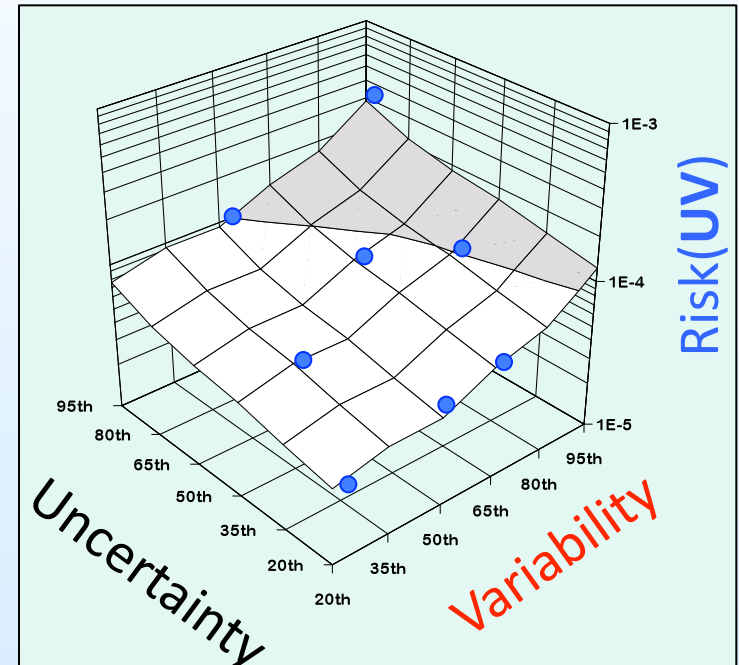
Outer, Uncertainty Loop



Yields Risk as a Function of Uncertainty and Variability

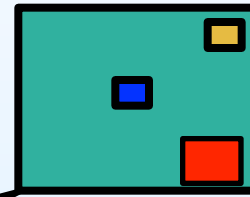
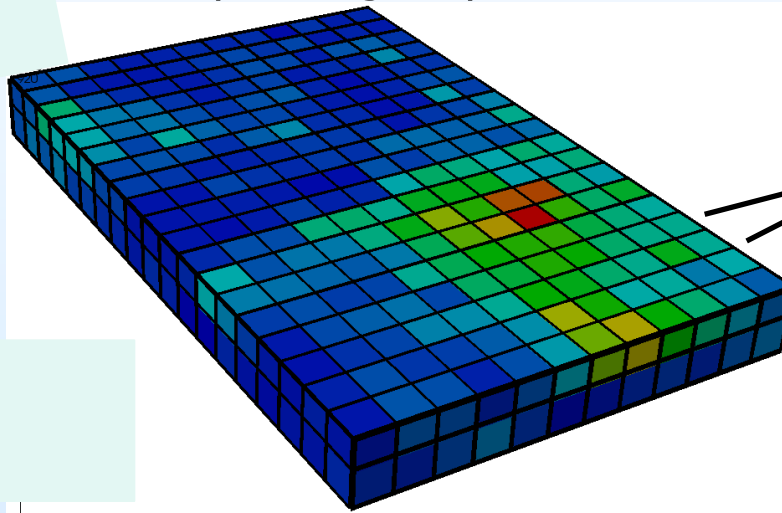
Example simulations show:

1. The specific metal mobilized in the event of CO₂ leakage greatly affects the outcome of risk
2. Hydrologic aquifer properties such as the degree of stratification and local dispersion greatly affect the magnitude and *distribution* (i.e. *uncertainty*) of risk
3. Risk is sensitive to the hydrologic flow parameters and warrants further examination in CCS risk assessment



Siirilla 2: Investigating how kinetic sorption and local dispersion influence risk.

1. Local (sub-grid) dispersion



$$Pe = \frac{v_x \lambda_{x=y}}{D_L} = \frac{\lambda_{x=y}}{\alpha_L}$$

2. Kinetic (rate-dependent) sorption

$$R_{LEA} = 1 + \frac{\rho_b K_d}{\theta} \longrightarrow K_d = \left[\frac{k_f}{k_r} \right] \longrightarrow R_{kin} = 1 + \frac{\rho_b}{\theta} \left[\frac{k_f}{k_r} \right]$$

Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications

Erica R. Siirila^{1,2} and Reed M. Maxwell^{1,2,3}

Received 17 October 2011; revised 20 January 2012; accepted 7 March 2012; published 25 April 2012.

[1] The interplay between regions of high and low hydraulic conductivity, degree of aquifer stratification, and rate-dependent geochemical reactions in heterogeneous flow fields is investigated, focusing on impacts of kinetic sorption and local dispersion on plume retardation and channeling. Human health risk is used as an endpoint for comparison via a nested Monte Carlo scheme, explicitly considering joint uncertainty and variability. Kinetic sorption is simulated with finely resolved, large-scale domains to identify hydrogeologic conditions where reactions are either rate limited (nonreactive), in equilibrium (linear equilibrium assumption is appropriate), or are sensitive to time-dependent kinetic reactions. By utilizing stochastic ensembles, effective equilibrium conditions are examined, in addition to parameter interplay. In particular, the effects of preferential flow pathways and solute mixing at the field-scale (macrodispersion) and subgrid (local dispersion, LD) are examined for varying degrees of stratification and regional groundwater velocities (v). Results show effective reaction rates of kinetic ensembles with the inclusion of LD yield disequilibrium transport, even for averaged (or global) Damköhler numbers associated with equilibrium transport. Solute behavior includes an additive tailing effect, a retarded peak time, and results in an increased cancer risk. The inclusion of LD for nonreactive solutes in highly anisotropic media results in either induced solute retardation or acceleration, a new finding given that LD has previously been shown to affect only the concentration variance. The distribution, magnitude, and associated uncertainty of cancer risk are controlled by the up scaling of these small-scale processes, but are strongly dependent on v and the source term.

Citation: Siirila, E. R., and R. M. Maxwell (2012), Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications, *Water Resour. Res.*, 48, W04527, doi:10.1029/2011WR011516.

An Expansive Sensitivity Analysis Was Conducted

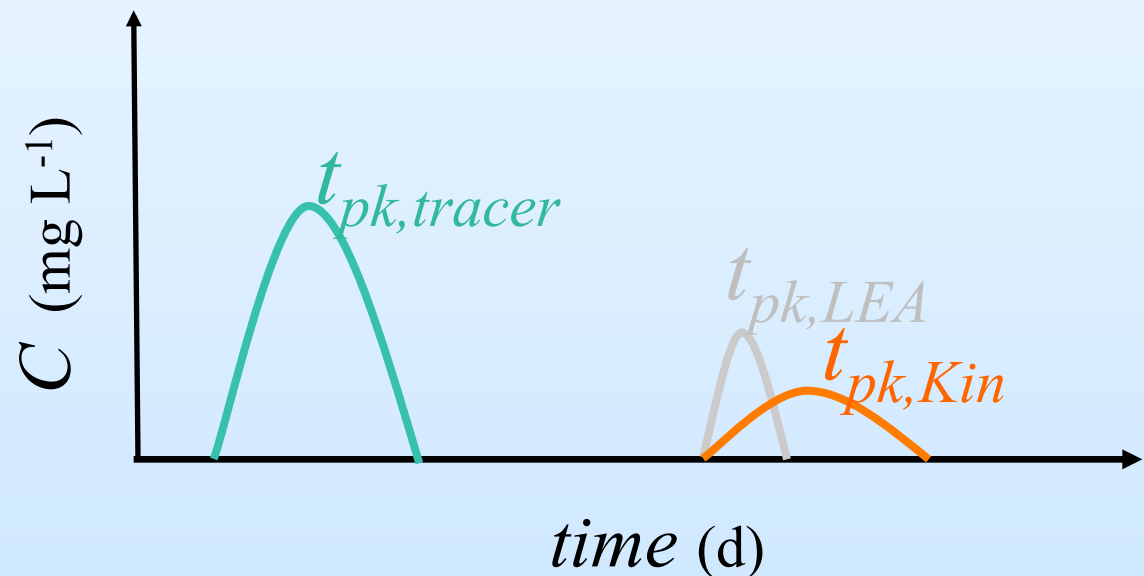
1. Sorption:
 - Equilibrium
 - Kinetic “slow”
 - Kinetic “fast”
 - Tracer
2. Local dispersion
 - $Pe = \infty$
 - $Pe \neq \infty$
3. Anisotropy
 - $\varepsilon = 0.1$
 - $\varepsilon = 0.006$
4. Mean groundwater velocity
 - $v = 0.001$ m/d
 - $v = 0.01$ m/d
 - $v = 0.1$ m/d
5. Continuous and pulse sources

96 ensembles

Per ensemble:

- 200 realizations
- 4 wells

76,800 BTCs
for statistical
analysis



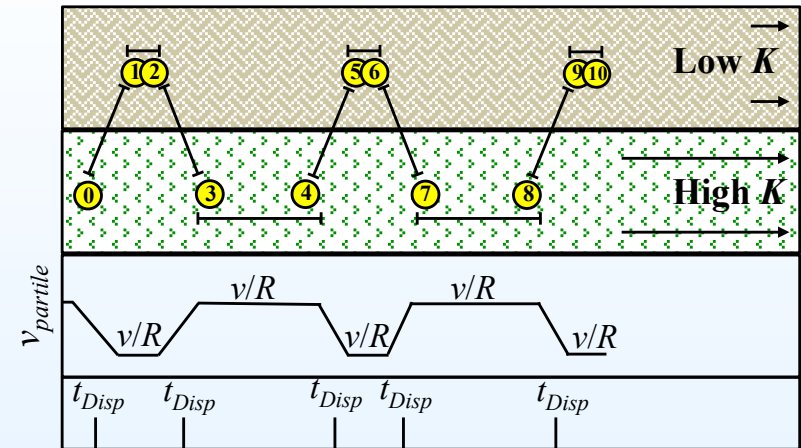
Significant Findings Include:

1. Even when equilibrium conditions were expected based on Da number (i.e. slow groundwater velocities), the effect of kinetic reactions is apparent

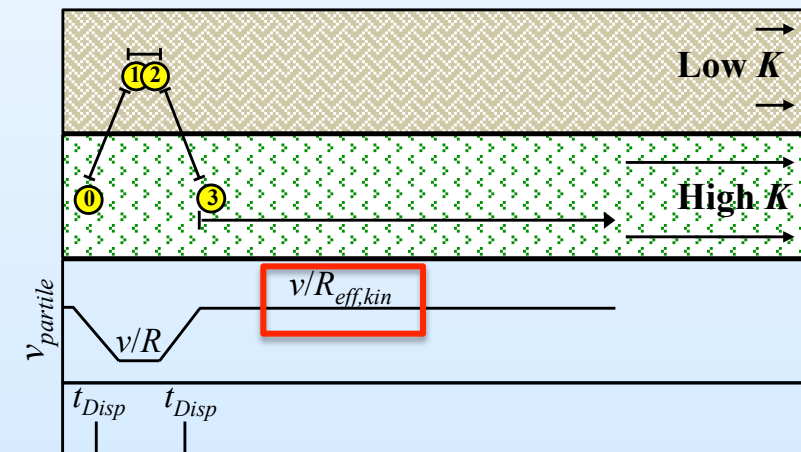
- Faster breakthrough, lower peak concentration, but more tailing
- *Higher overall risk*

2. The inclusion of local dispersion in non-sorbing solutes (i.e. a tracer) yields either apparent retardation or acceleration when the simulated aquifer is highly anisotropic – higher calculated risk

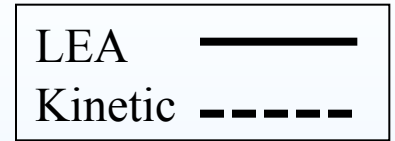
Equilibrium Scenario



Kinetic Scenario

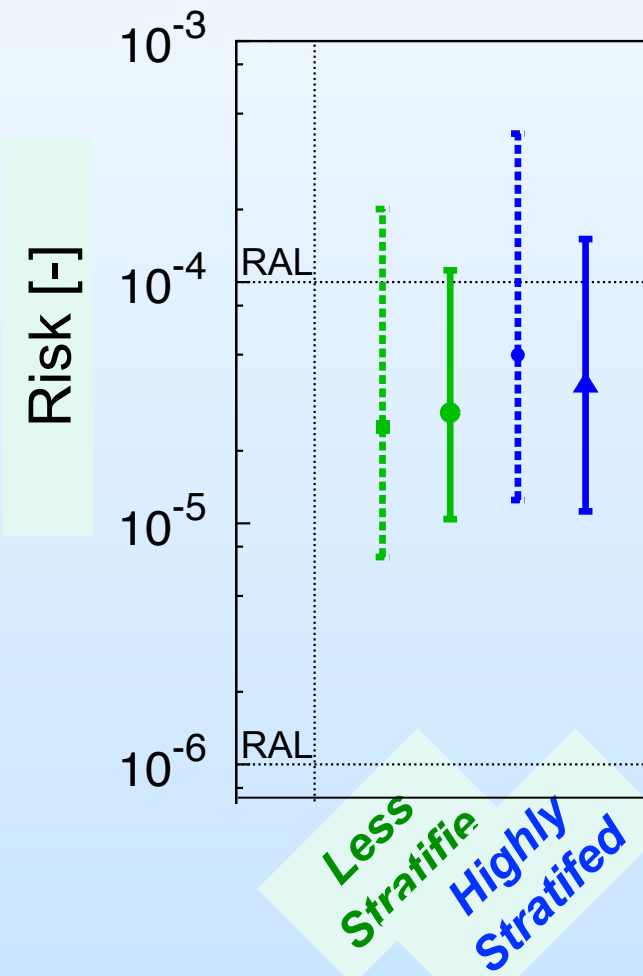
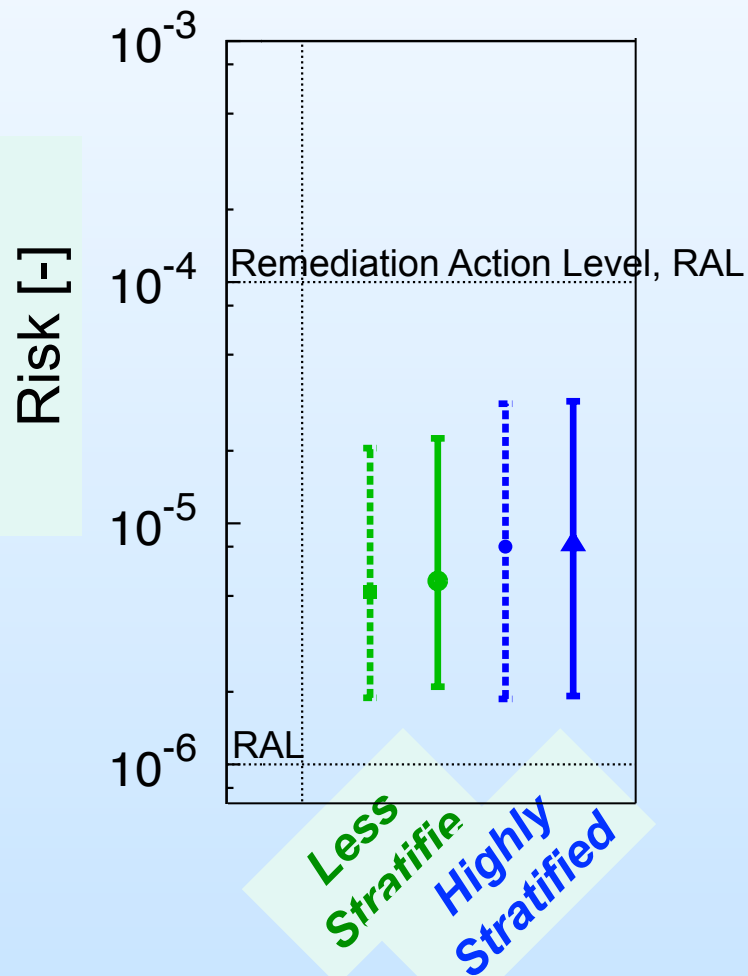


Implications: Carcinogenic, Human Health Risk

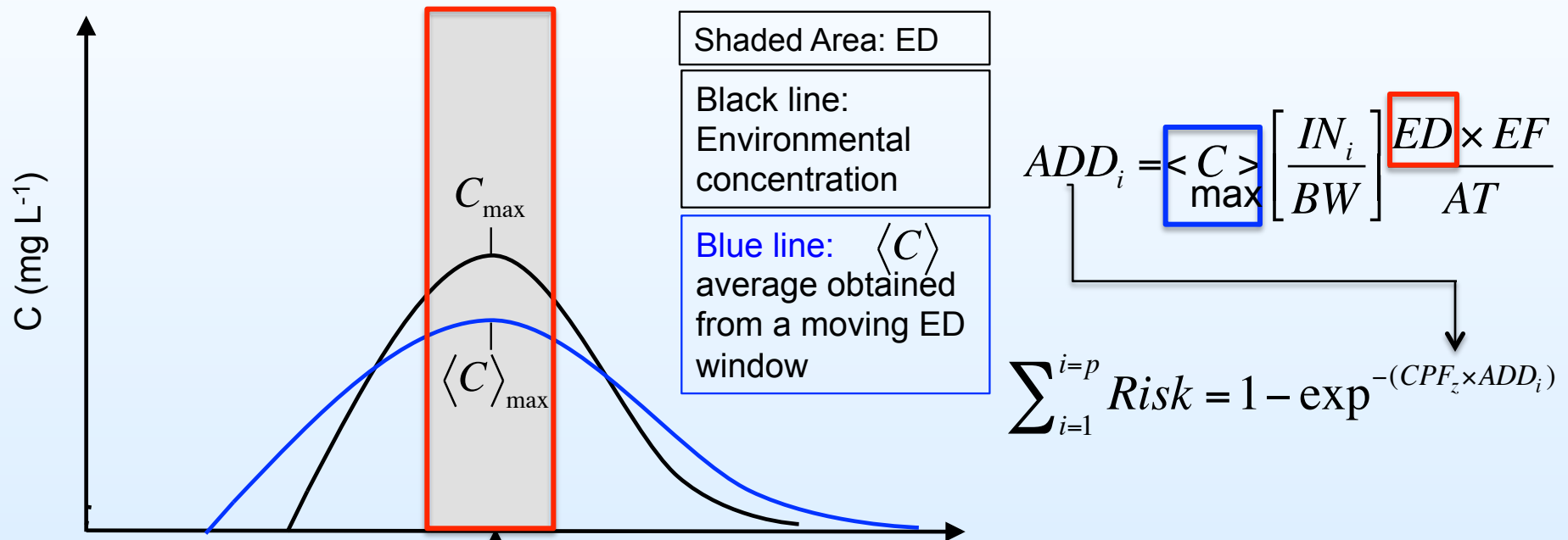


Excluding Local Dispersion ($Pe=\infty$)

Including Local Dispersion



Siirilla 3: The Development of a Time Dependent Risk Assessment (TDRA) framework



Risk is only calculated during this time of contamination

Question1: How can risk outside of this Exposure Duration (ED) window influence an assessment?

Question2: How does the assessment change given varying concentration signals?

Question3: How is risk affected by the size of the ED window?



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Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



A new perspective on human health risk assessment: Development of a time dependent methodology and the effect of varying exposure durations

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ABSTRACT

We present a new Time Dependent Risk Assessment (TDRA) that stochastically considers how joint uncertainty and inter-individual variability (JUV) associated with human health risk change as a function of time. In contrast to traditional, time independent assessments of risk, this new formulation relays information on when the risk occurs, how long the duration of risk is, and how risk changes with time. Because the true exposure duration (ED) is often uncertain in a risk assessment, we also investigate how varying the magnitude of fixed size durations (ranging between 5 and 70 years) of this parameter affects the distribution of risk in both the time independent and dependent methodologies. To illustrate this new formulation and to investigate these mechanisms for sensitivity, an example of arsenic contaminated groundwater is used in conjunction with two scenarios of different environmental concentration signals resulting from rate dependencies in geochemical reactions. Cancer risk is computed and compared using environmental concentration ensembles modeled with sorption as 1) a linear equilibrium assumption (LEA) and 2) first order kinetics (Kin). Results show that the information attained in the new time dependent methodology reveals how the uncertainty in other time-dependent processes in the risk assessment may influence the uncertainty in risk. We also show that individual susceptibility also affects how risk changes in time, information that would otherwise be lost in the traditional, time independent methodology. These results are especially pertinent for forecasting risk in time, and for risk managers who are assessing the uncertainty of risk.

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Using two contamination scenarios, TDRA yields

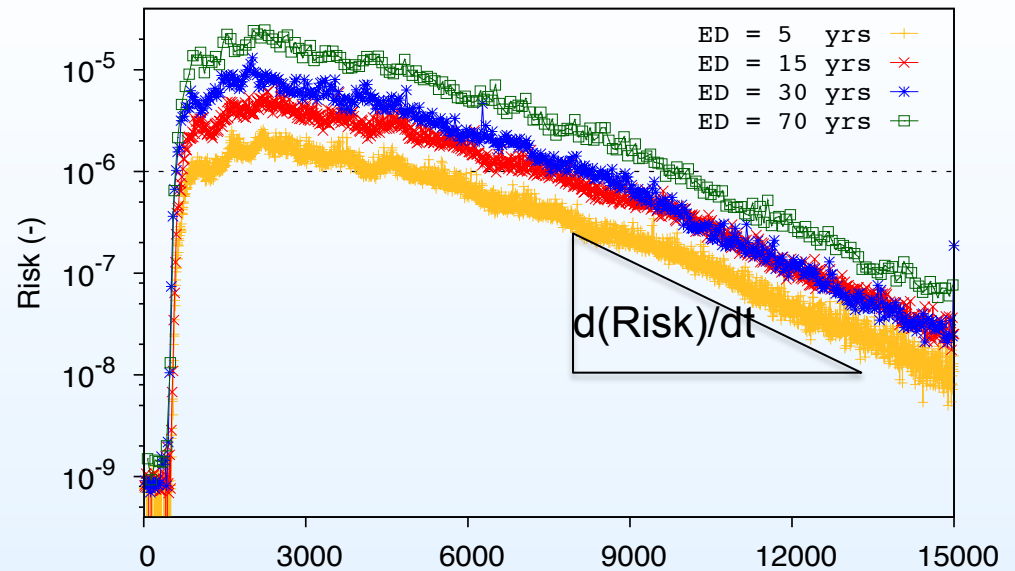
1. Information on how risk changes as a function of time: $d(\text{Risk})/dt$
2. A comparison of risk duration versus magnitude

Percent of time over the RAL:

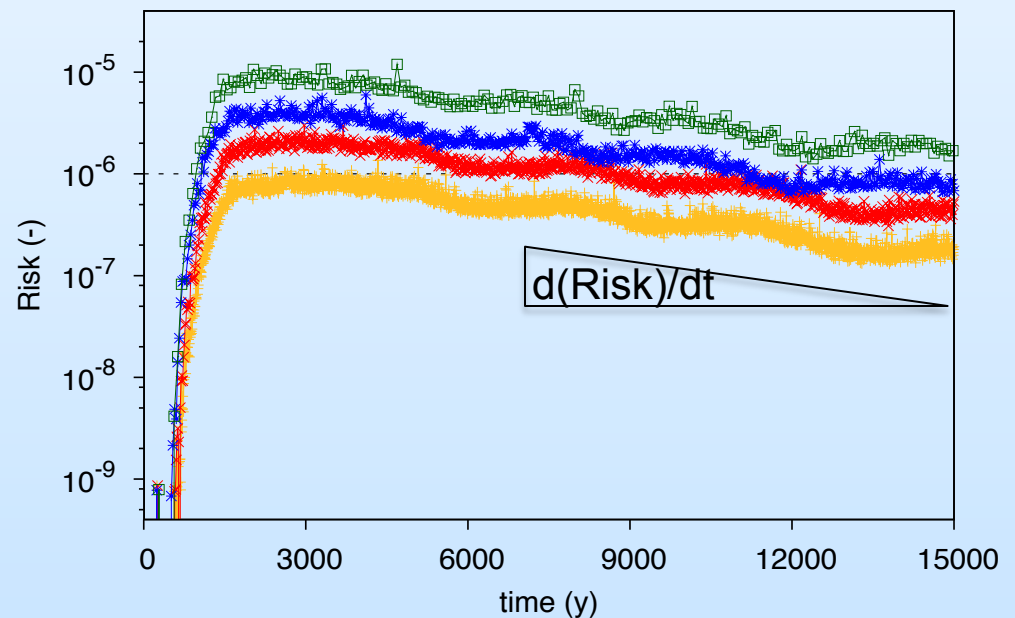
- Scenario 1: 63%
- Scenario 2: 93%

Consider higher risk over a shorter period of time? Or a lower risk over a longer period of time?

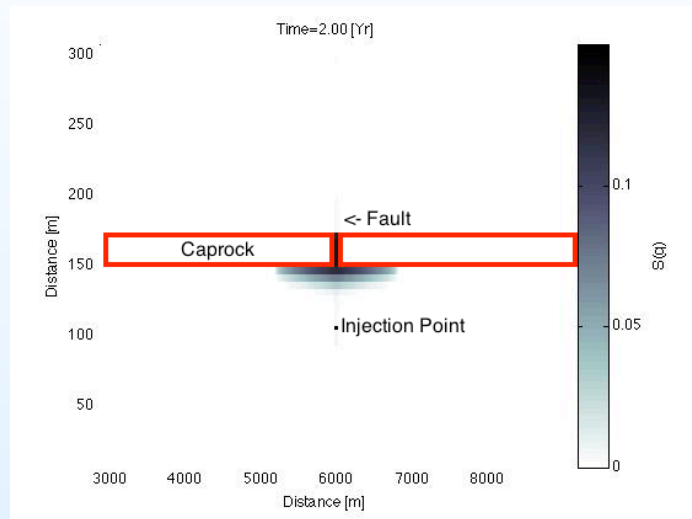
Risk Scenario 1



Risk Scenario 2



Menke: Numerical multiphase simulations to investigate leakage through a fault

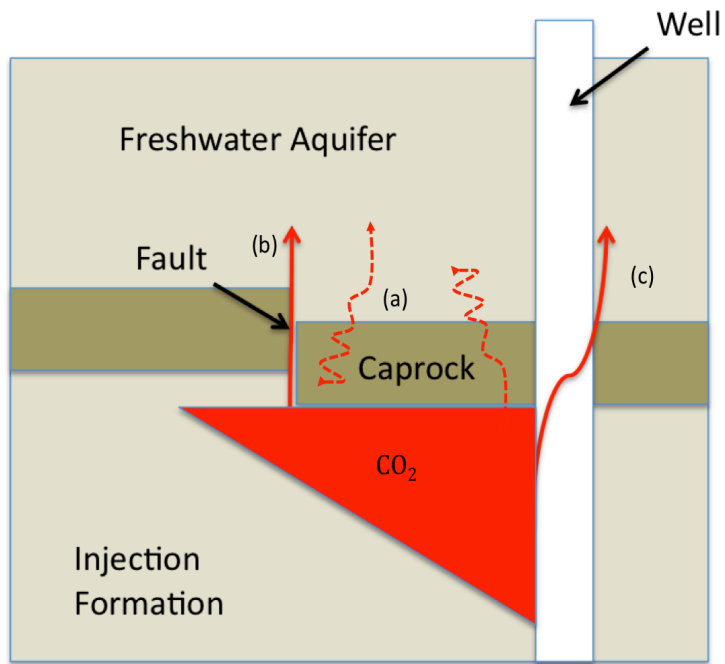


Recently, won the best student presentation at the Front Range Consortium for Research Computing Symposium

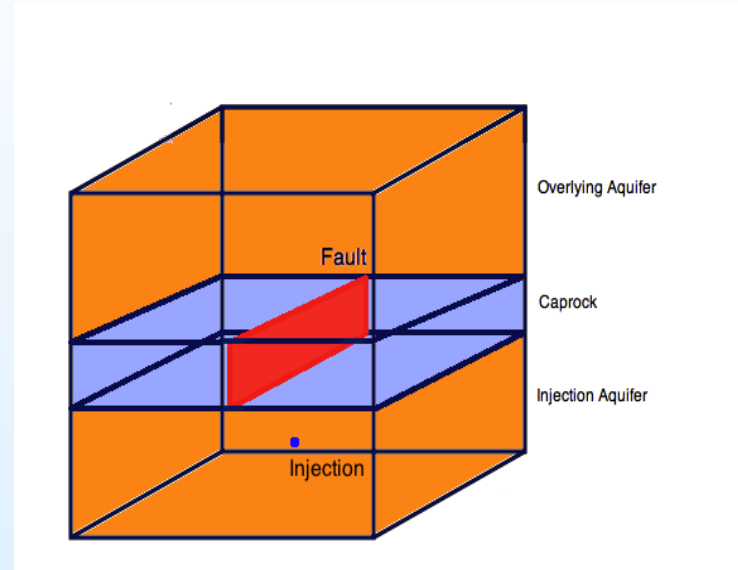
High Performance Computing:

- Conducted at Golden Energy Computing Organization (GECO).
- Simulations run for 3 years of injection, then 0.5 years for pressure/saturation equilibration.
- > 1,000,000 degrees of freedom in each simulation
- 1 simulated year of CO₂ injection: ~10 days (wall-clock time) on 128 processors (30,700 CPU hrs)
- Suite of simulations used approx 1,500,000 CPU hrs

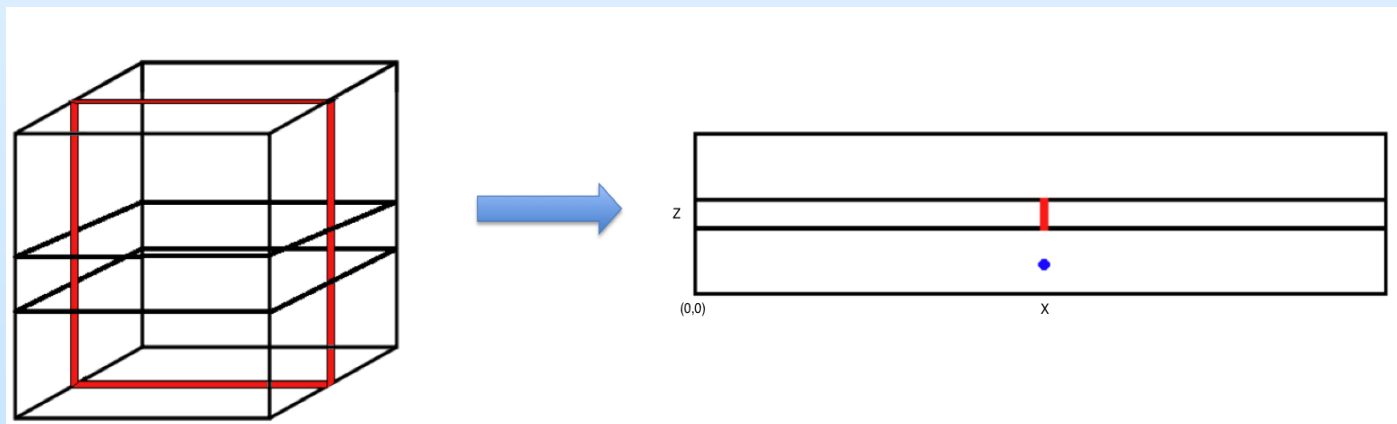
Leakage Pathways:



Conceptual Model:



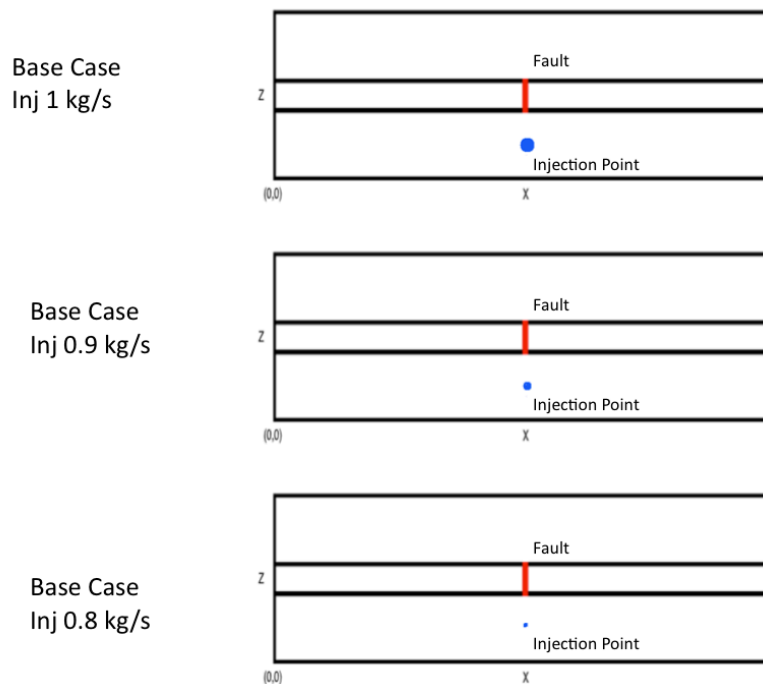
Numerical Model: PFlowTran (LANL)



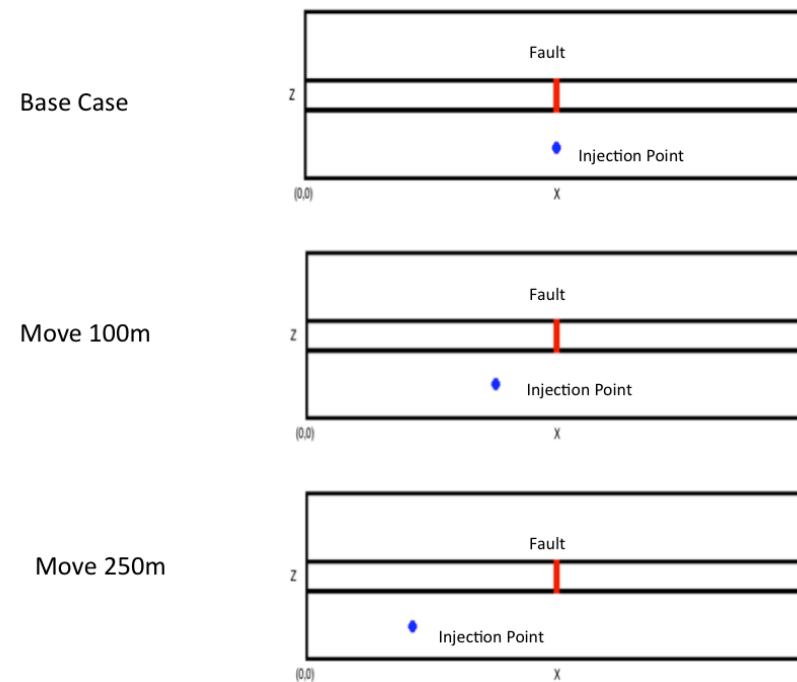
Base Case and Variation of Parameters:

- Base Case created from known literature values.
- Varied parameters to try and understand leakage constraints:
 - Injection Points Horizontal Distance from Fault
 - Injection Rate
 - Fault Permeability

Variation of Injection Rate



Variation of Horizontal Distance of the Fault from the Injection Point



Base Case Parameter	Value
Fault Perm	$1 \times 10^{-12} \text{ m}^2$
Caprock Perm	$1 \times 10^{-19} \text{ m}^2$
Formation Perm	$1 \times 10^{-9} \text{ m}^2$
Injection Rate	1 kg/s
Fault Dimensions [x,y,z]	5m x 10m x 25m

Case:	Base	2 [inject 100m from fault]	3 [inject 250m from fault]	4 [Inj 0.9 kg/s below fault]	5 [Inj 0.8 kg/s below fault]
<i>CO₂ Breakthrough Time [Yr]</i>	< 0.1	< 0.2	< 0.3	0.1	0.2
<i>Avg H₂O Leakage rate [kg/yr]</i>	2.67×10^6	3.12×10^6	3.92×10^6	1.63×10^6	2.84×10^6
<i>Avg CO₂ Leakage rate [kg/yr]</i>	1.19×10^6	1.09×10^6	9.74×10^5	1.01×10^5	7.79×10^5
<i>Max H₂O Leakage rate [kg/yr]</i>	1.16×10^7	1.16×10^7	1.16×10^7	2.62×10^6	9.32×10^6
<i>Max CO₂ leakage Rate [kg/yr]</i>	1.61×10^6	1.45×10^6	1.23×10^6	1.31×10^6	1.03×10^6
<i>Total H₂O Leaked [kg]</i>	7.94×10^6	9.26×10^6	1.18×10^7	8.05×10^6	8.51×10^6
<i>Total CO₂ Leaked [kg]</i>	3.58×10^6	3.17×10^6	2.73×10^6	2.91×10^6	2.18×10^6

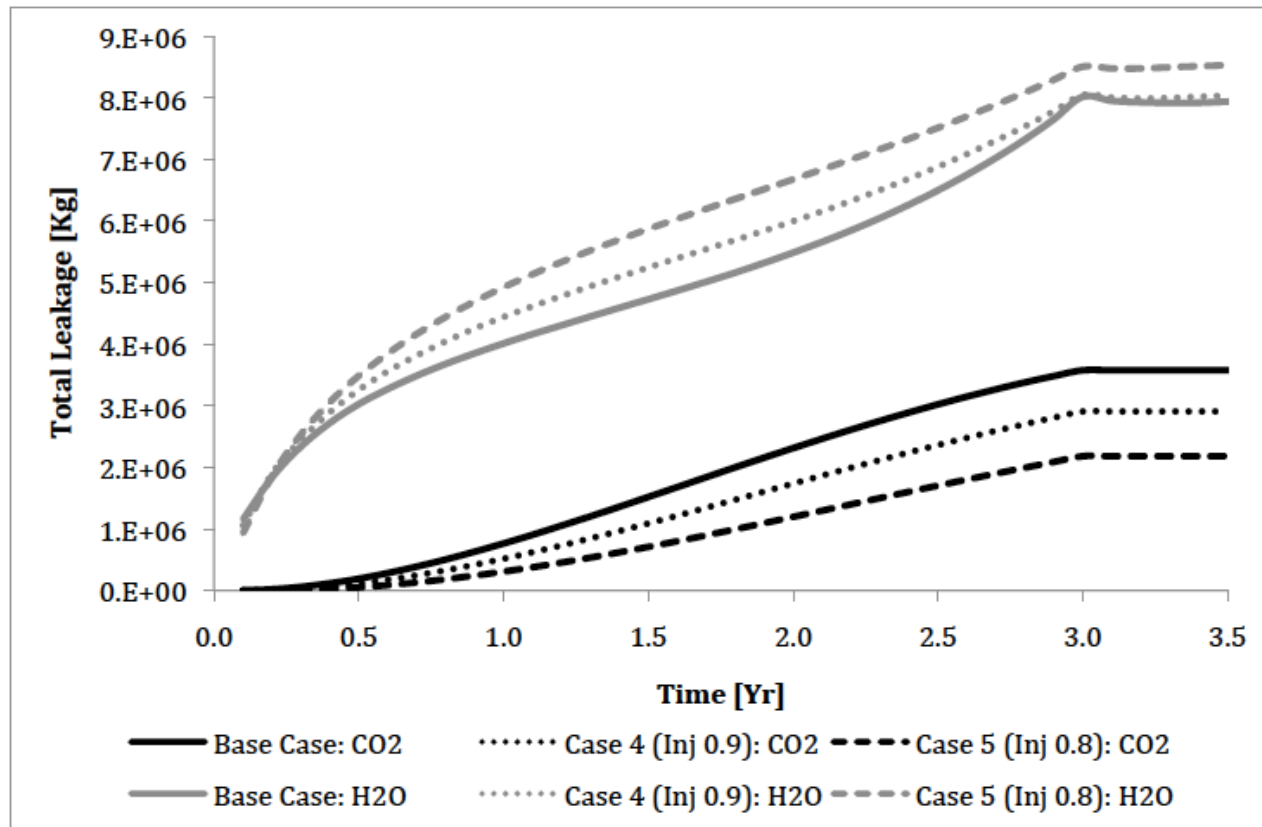


Figure 3.10: Total Leakage of CO₂ and H₂O in kg when the injection rate is varied.

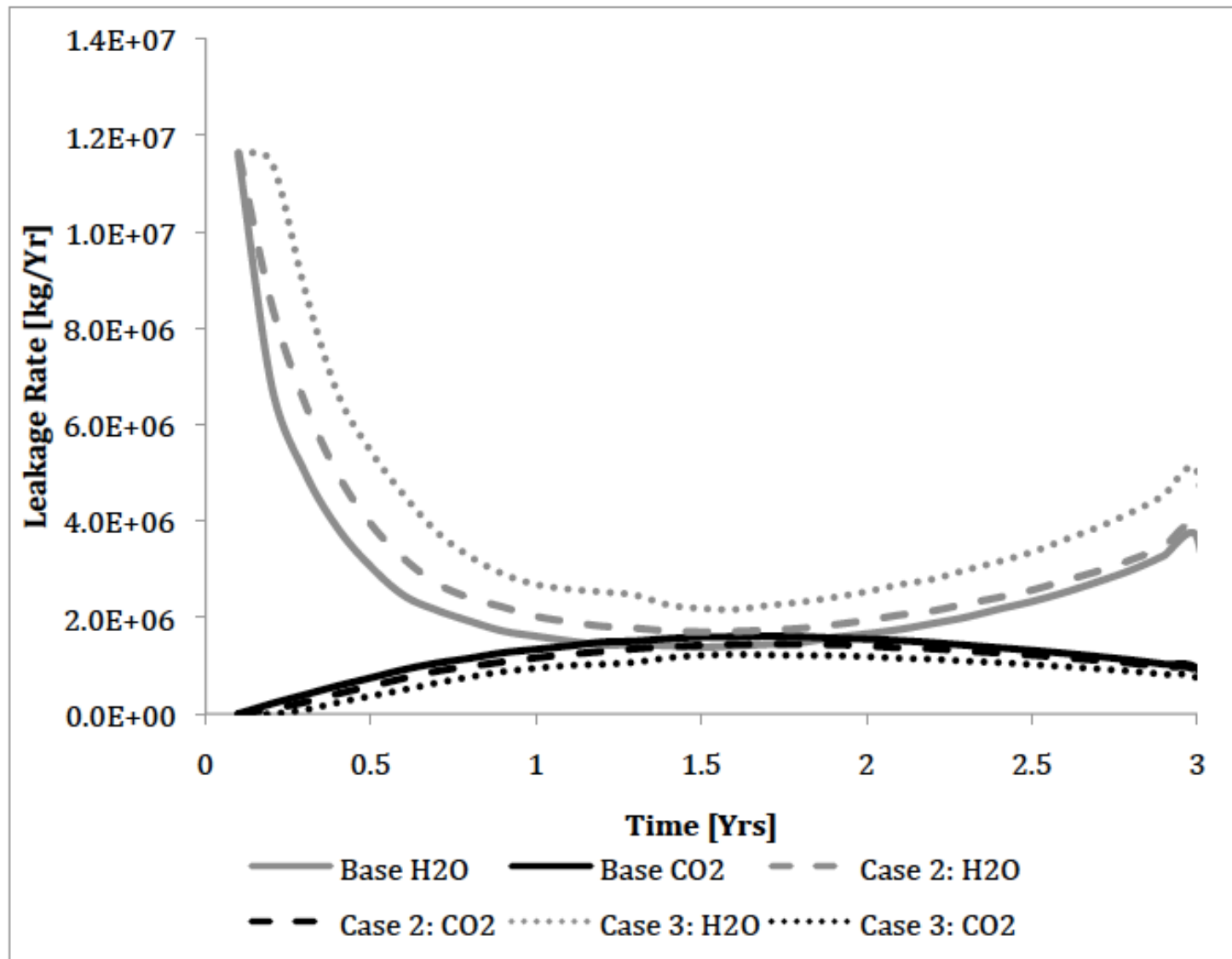


Figure 3.6: Leakage rate in kg/yr is plotted as a function of time for the base case and cases 2 & 3. As the injection point is moved away from the fault the CO₂ leakage rate falls and the H₂O leakage rate increases.

Menke: Findings

- Brine leakage may increase for conditions where CO₂ leakage decreases (lower injection pressures, further distance from fault) due to relative permeability considerations
- Reduction in buoyancy (denser SC CO₂) at larger times can cause decreases in CO₂ leakage and increases in brine leakage
- Leakage rates do not scale linearly with injection rates, permeability, and distance from the fault.
- If a leak is detected, leakage can be stopped “relatively quickly” by turning off injection (fast ramp down).

Kirsch: Dissolution Experiments with *Siliclastic Rocks*

To investigate the geochemical response of sandstone aquifers to CO₂ leakage



Outcrop of the Mesaverde Group

Samples were collected from outcrop of the Mesaverde Group in northwestern Colorado in Routt County.

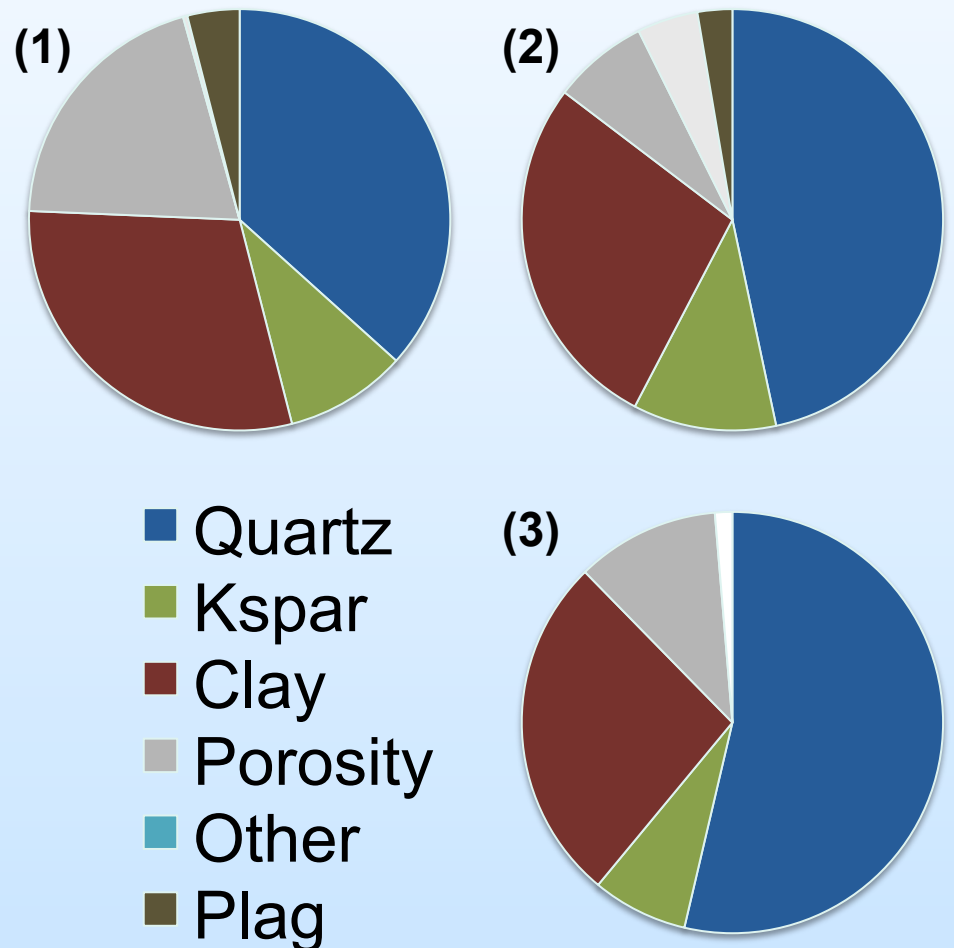
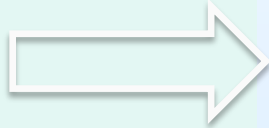
These sandstones currently yield water to wells for local domestic and agricultural purposes, and have the potential for increased groundwater development in a water-scarce future.



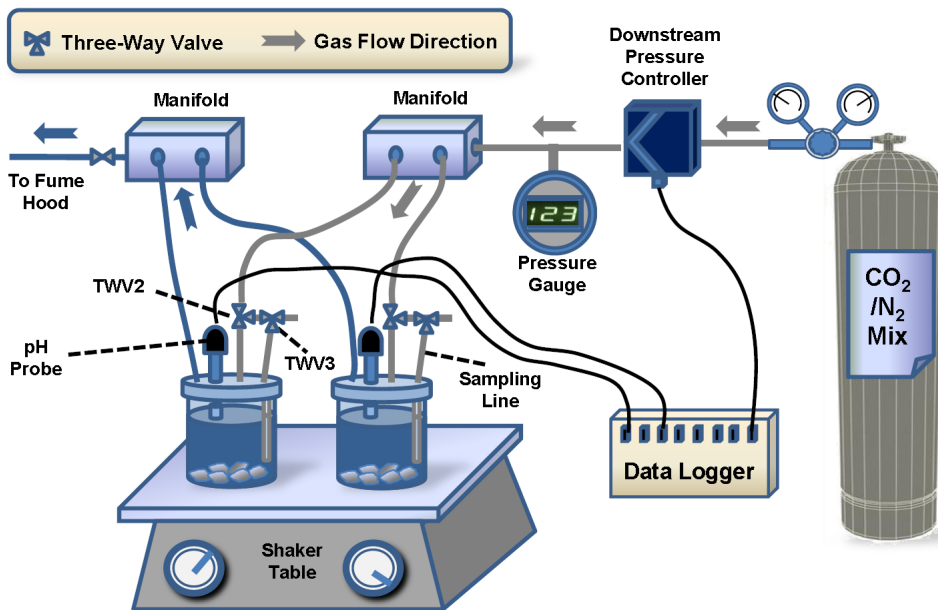
Which minerals are likely controlling the aqueous concentration of trace metals?

Rock Characterization:

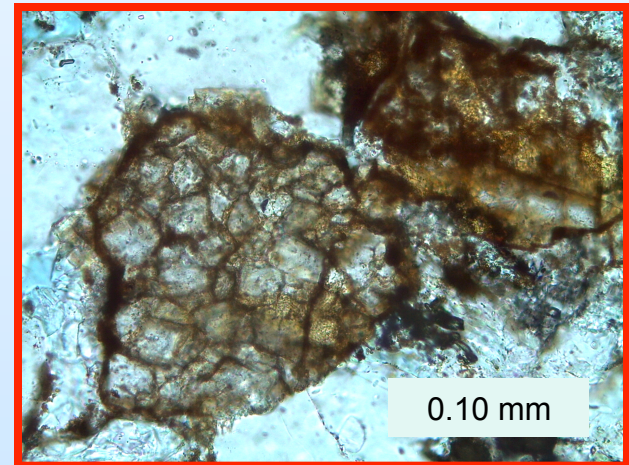
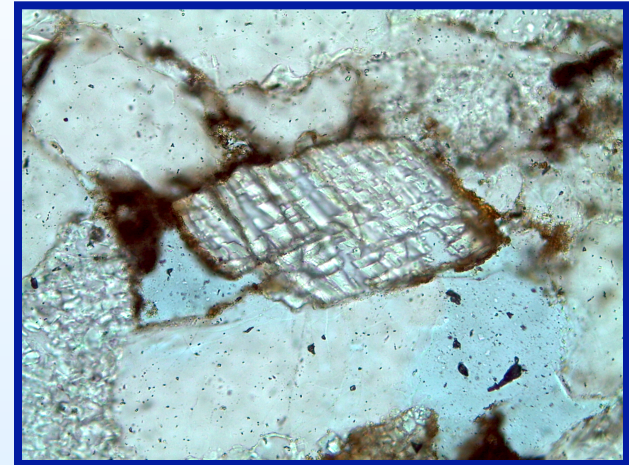
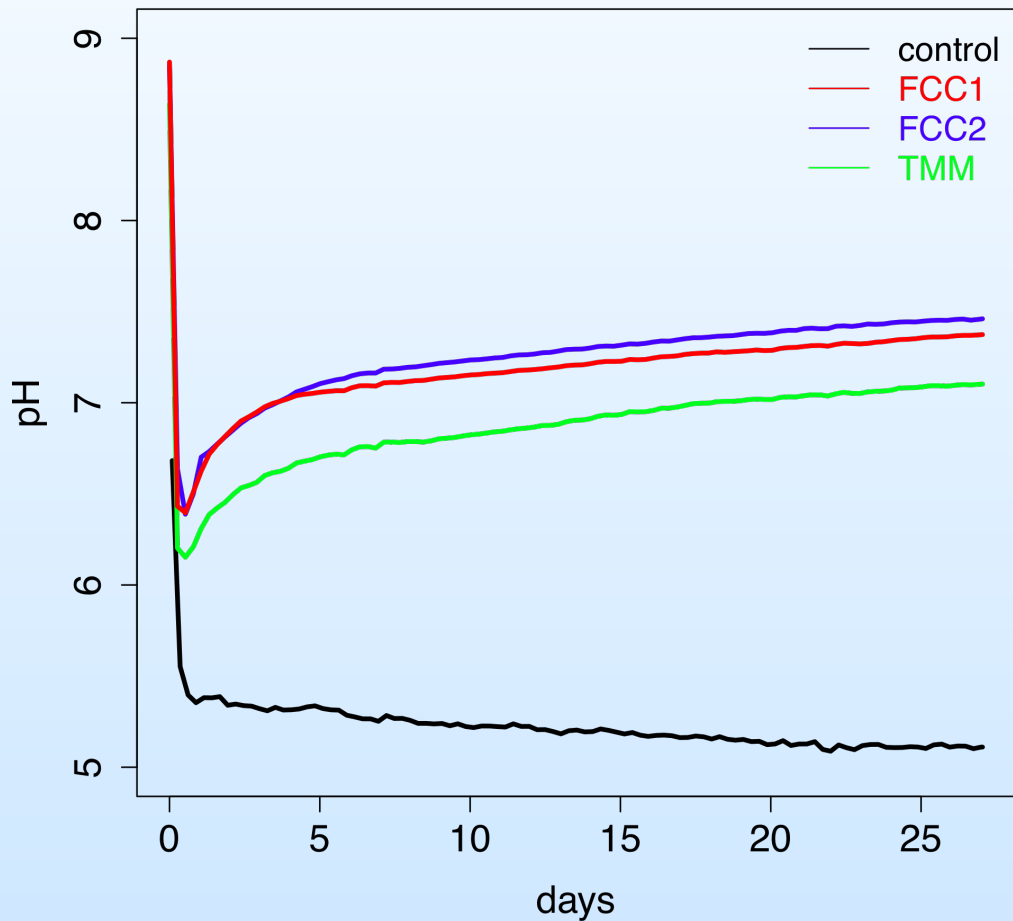
- Point count
- Whole rock
- XRD
- BET surface area
- Sequential extraction
- SEM/EDX



Experiments: How does the fluid composition and microbiology change with time at elevated CO₂ partial pressures?



Results so far: Dissolution of silicate rock can buffer pH



Summary: Lessons Learned

- Aquifer heterogeneities are important in risk calculations
- Kinetic reactions with local dispersion can result in lower peak concentrations, but earlier arrival and longer tails, thus higher calculated risk
- Temporal risk calculated considering longer exposure durations with smaller concentrations important in evaluating the true risk
- Brine leakage may increase for conditions where CO₂ leakage decreases (lower injection pressures, further distance from Fault) due to relative permeability-pressure considerations
- If a leak is detected, leakage can be stopped “relatively quickly” by turning off injection (fast ramp down).
- Typical sandstone minerals can buffer acidity during leakage into aquifers

Summary: Future Work

- Siirilla to complete PhD dissertation.
- Menke successfully defend thesis
- Complete paper on multiphase simulations of leakage through faults.
- Complete experiments, evaluate metal release and impact on microbes from sandstones at typical aquifer pressures.
- Kirsch to complete M.S. Thesis
- Complete paper on experiments.

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- Siirila, E.R., Maxwell, R.M., 2012, A new perspective on human health risk assessment: Development of a time dependent methodology and the effect of varying exposure durations: *Science of the Total Environment*, v. 431, p. 221-232, available at: <http://www.sciencedirect.com/science/article/pii/S0048969712007097>.
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Menke, H., 2012. Evaluating storage of geologically sequestered CO₂ using numerical simulations, M.S. Thesis in Environmental Science and Engineering, Colorado School of Mines, Golden CO.

Siirilla, E.R., 2012. A quantitative methodology to assess the risks to human health from CO₂ leakage into groundwater, M.S. Thesis in Hydrologic Science and Engineering, Colorado School of Mines, Golden CO.

Abstracts

More than 15:

American Geophysical Union Fall Meeting

Geological Society of America Annual Meeting

ASCE Environmental Water Resources Institute Annual Meeting

Goldschmidt Meeting on Geochemistry

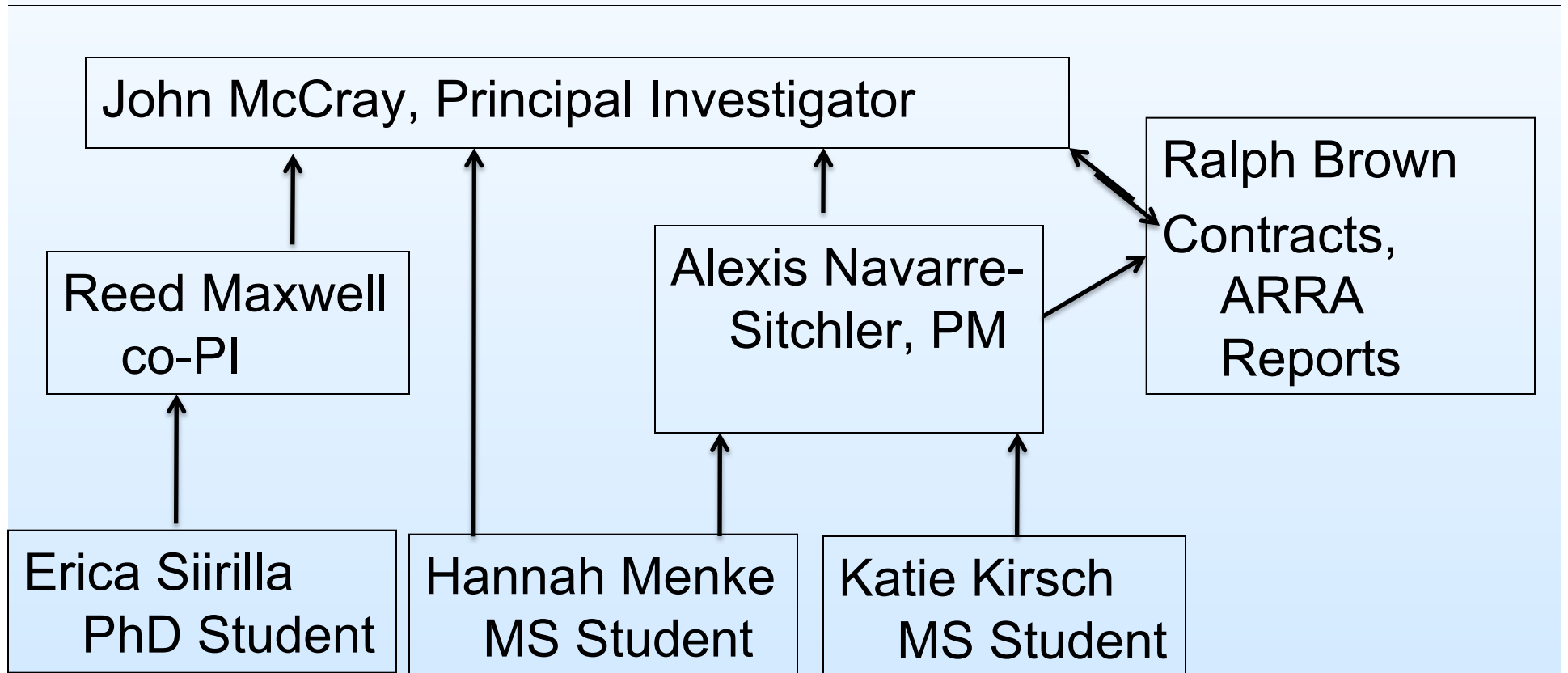
National Ground Water Association Summit

Questions?



Appendix

Organization Chart



Project Overview: Goals and Objectives : Milestones

Task/ Subtask #	Project Milestone Description	Project Duration - Dec 2009 - Nov 2012													Planned Start Date	Planned End Date	Actual Start Date	Actual End Date	Comments
		FY 2010				FY 2011				FY 2012				FY 13					
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13					
1.2	A - Project Kickoff meeting	■													12/1/09	12/31/09	12/1/09	12/31/09	Completed as planned
1.2	B - Educational Program Instituted		■	■											1/1/10	6/30/10	1/1/10	1/30/10	Completed ahead of schedule
1.2	C - Semi-Annual Progress Report				■										9/1/10	9/30/10	7/1/10	7/31/10	Quarterly report for Q3 - 2010 FY serves as semi-annual report per email from Joshua Hull
1.2	D - Yearly Review Meeting						■								11/1/11	11/1/11	11/1/11	11/1/11	Participation in NETL webinar
1.2	E - Yearly Review Meeting										■				9/30/12	9/30/12			
2.3	F - Determine most probable leakage scenarios			■	■										4/1/10	6/30/10	4/1/10	6/30/10	Completed as planned
2.2	G - List of EPA-regulated byproducts of reaction between aquifer materials and CO2			■	■										4/1/10	12/31/10	4/1/10	9/30/10	Completed ahead of schedule
3.1	H - Initial characterization of injection and caprock formation begun		■	■											1/1/10	12/31/10	1/1/10	12/31/10	Completed as planned
4.1	I - Development of course syllabus complete														12/1/10	8/15/11	11/1/10	8/1/11	Completed as planned
2.3	J - Identify and rank aquifer sites for use in risk simulations complete			■	■	■									7/1/10	3/31/11	1/1/10	3/31/11	Completed as planned
2.3	K - Identify and rank aquifer-leakage scenarios for use in risk simulations complete					■	■								10/1/10	6/30/11	10/1/10	6/30/11	Completed as planned
3.2	L - Determine rate parameters of important geochemical reactions				■	■	■								7/1/10	6/30/11	7/1/10	6/30/11	Completed as planned
4.3	M - Summary on demographics and grades for the university course										■				6/1/11	12/31/11	8/1/11		in progress
2.4	N - Complete screening risk assessment simulations										■	■			7/1/11	6/30/12	7/1/11	6/30/12	Completed as planned
3.4	O - Complete geochemical modeling for relevant carbon injection scenarios													■	10/1/11	11/30/12	10/1/11		in progress
2.4	P - Complete primary risk simulations for aquifer leakage												■	■	7/1/12	11/30/12	7/1/11		in progress