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Shallow Groundwater Study at the Cranfield site

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Acknowledgements

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SECARB Southeast Regional Carbon Sequestration Partnership · NETL · Southern States Energy Board · Water Research Foundation · Advanced Resources International, Inc. · EPRI · Southern Company · Denbury

Jackson School of Geosciences · Bureau of Economic Geology · Gulf Coast Carbon Center · ICET Institute for Clean Energy Technology Mississippi State University · Anchor QEA

Cranfield, Mississippi

- Located 15 miles east of Natchez, MS
- The oil field discovered in 1940s and abandoned in 1960s

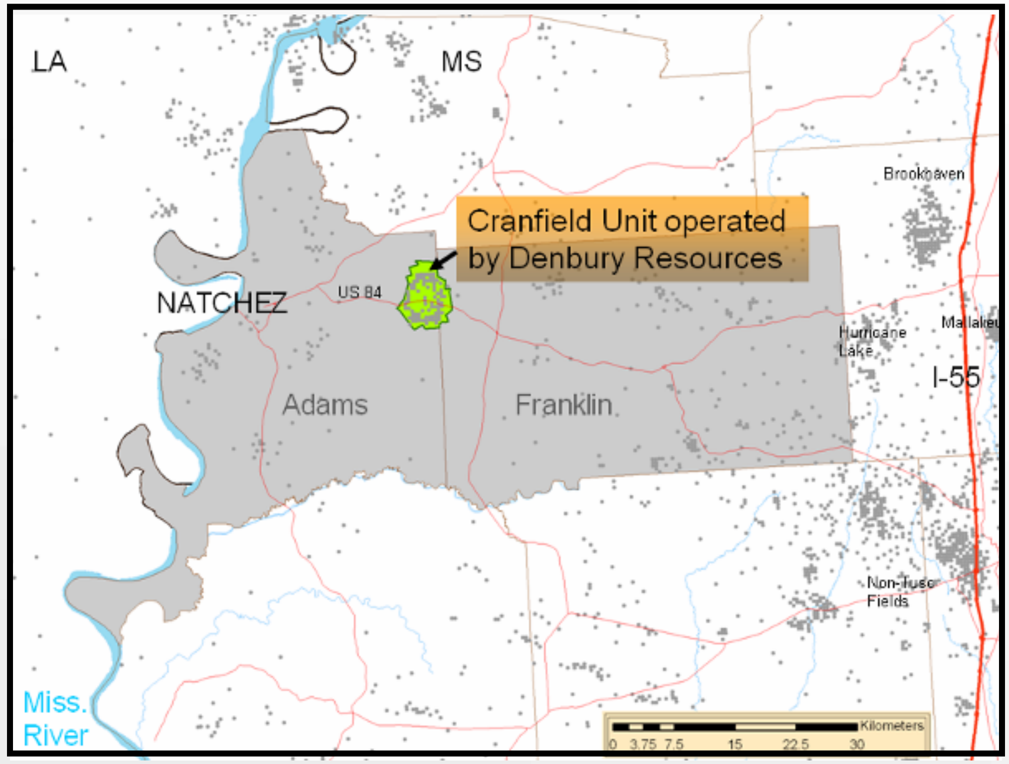
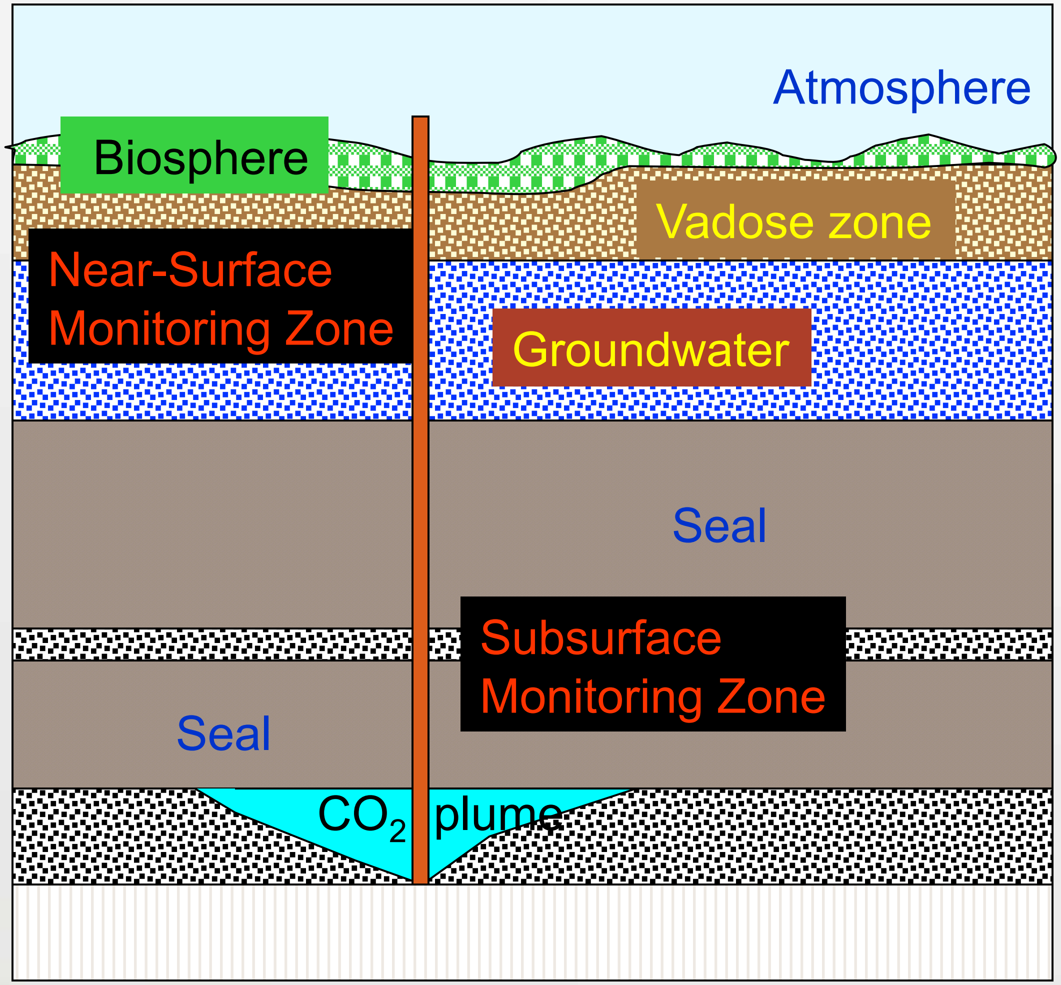


Figure courtesy of Tip Meckel

- Currently owned and operated by Denbury Resources
- Injection of CO_2 for EOR since 2008



Objectives

- To evaluate plausibility of groundwater chemistry monitoring for detecting CO_2 leakage
- To assess potential impacts of groundwater quality in case of CO_2 leakage

Stepwise groundwater monitoring strategy

Step 1. Characterize shallow groundwater chemistry and mineralogy of aquifer sediments

Step 2. Identify a set of geochemical parameters for detecting CO_2 leakage

Step 3. Test & validation

- Numerical modeling
- Lab experiments
- Field controlled-release experiments (Push-pull tests)

Step 4. Application

Groundwater chemistry monitoring for detecting CO_2 leakage

Research team

- Main participants
  - Bureau of Economic Geology (BEG)
    - Data analysis
    - Lab experiments
    - Field controlled-release tests
    - Numerical modeling
  - University of Mississippi
    - Groundwater sampling
  - Mississippi State University
    - Water chemistry analysis
  - Anchor QEA
    - Reactive transport modeling in a regional shallow aquifer

Tasks completed

- Characterization of groundwater chemistry at the Cranfield shallow aquifer
- Lab batch experiments of water-rock-CO_2 interactions
- Field controlled-release tests at the Cranfield site
- Numerical modeling

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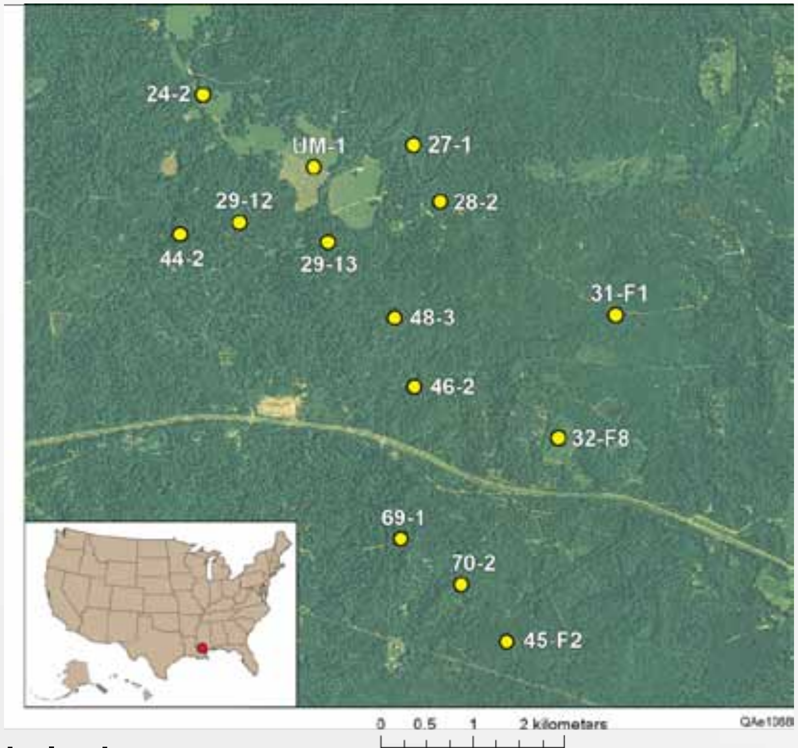
Characterization of groundwater chemistry

- 10 field campaigns for groundwater sampling since August, 2008
  - On-site measurements: pH, temperature, alkalinity, water level
  - Lab analysis: Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Pb, Se, Zn, F^-, Cl^-, SO_4^{2-}, Br^-, NO_3^-, PO_4^{3-}, TOC, DIC, pH, Alkalinity, VOC, δC13 of DIC

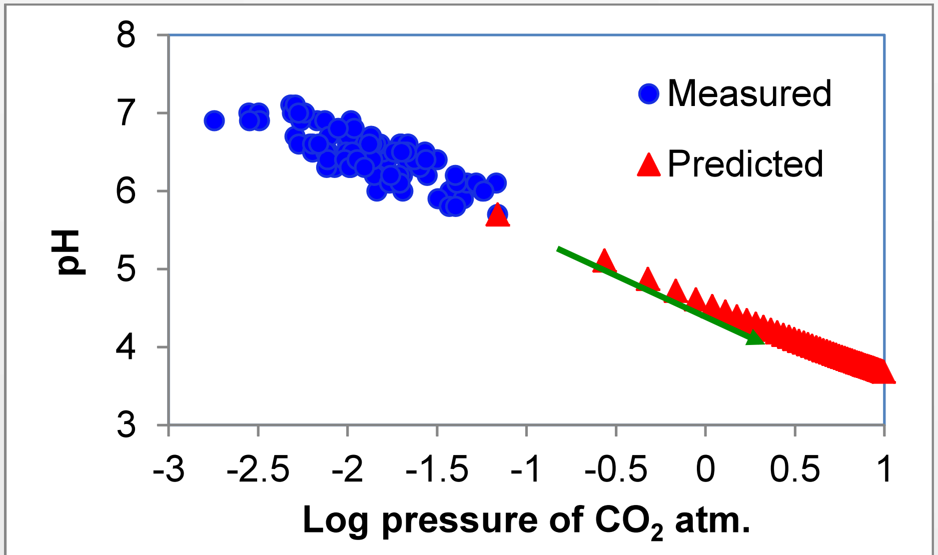


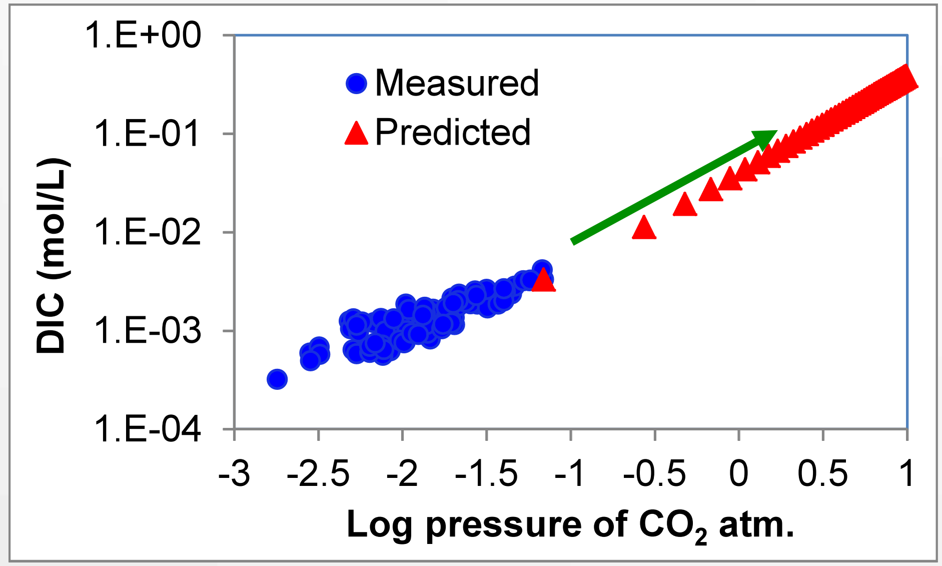
- X-RD analysis of sedimentary samples indicates that silicates and clay minerals are dominant
- Groundwater chemistry dominated mainly by silicate mineral weathering
- Carbonate parameters (e.g., DIC), pH, and δC13 of DIC may be used for detecting CO_2 leakage at the Cranfield site

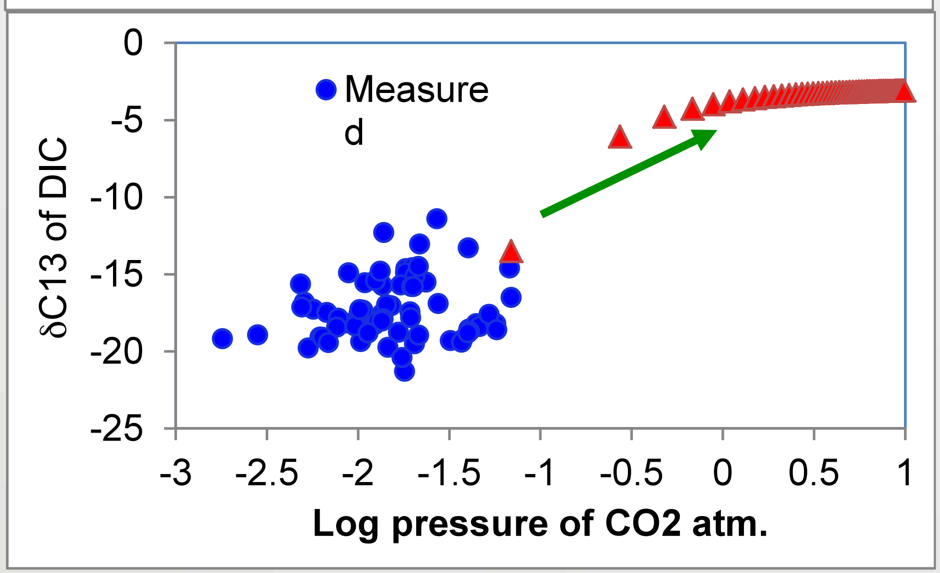
Changbing Yang, Katherine Romanak, Susan Hovorka, Rober Holt, Jeff Lindner, and Ramon Trevino, Near-surface monitoring of large-volume CO2 injection at Cranfield: early field test of SECARB phase III, SPE Journal, in Press

Numerical Modeling

Geochemical modeling







Simulating CO_2 leakage into the Cranfield-type shallow aquifers as CO_2 pressure builds up:

- pH will be lowered
- DIC will increase
- δC13 of DIC will approach -3‰, the value of δC13 of CO_2 injected

Laboratory batch experiments of water-rock-CO_2 interactions

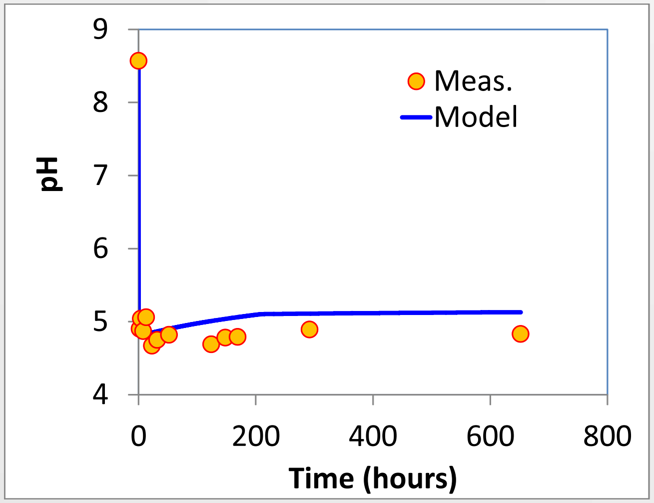
To understand responses of groundwater chemistry to CO_2 leakage under laboratory conditions

- 106 g of sedimentary samples and 420 ml groundwater from the Cranfield shallow aquifer
- bubbled with Ar for a week, then with CO_2 for ~half year

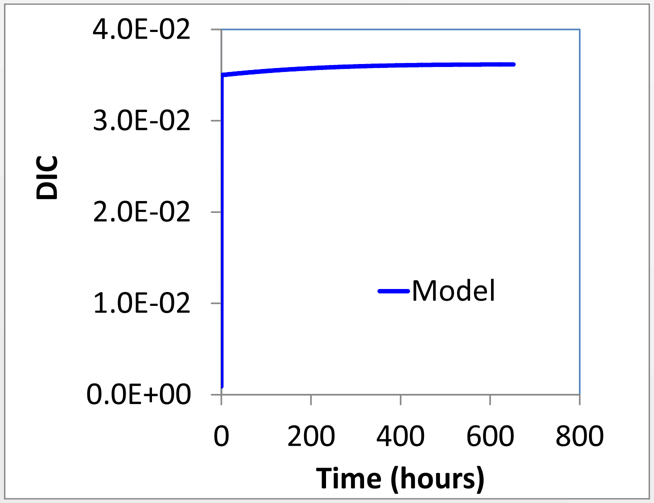
Laboratory batch experiments of water-rock-CO_2 interactions

Results

pH



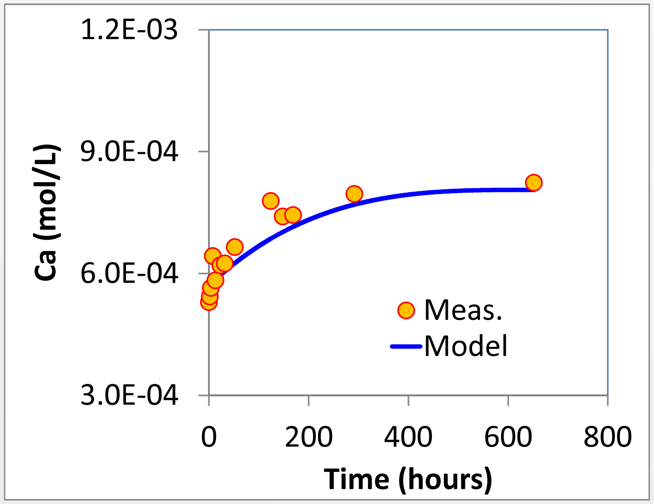
DIC

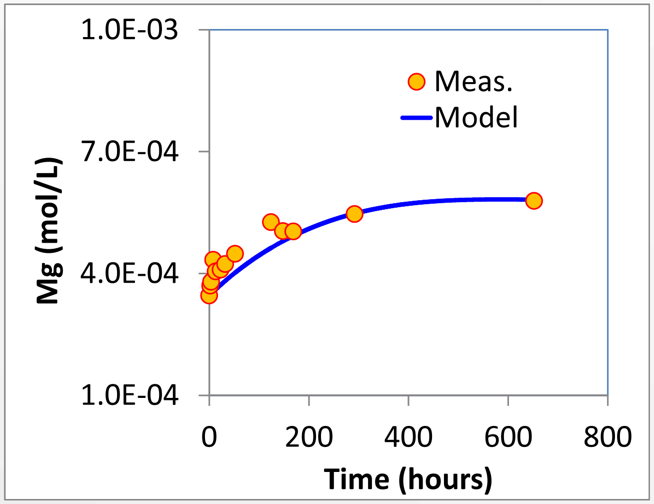


Laboratory batch experiments of water-rock-CO_2 interactions

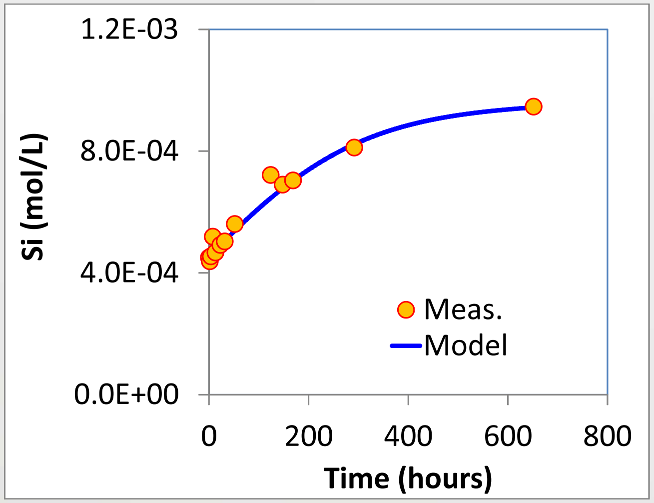
Results

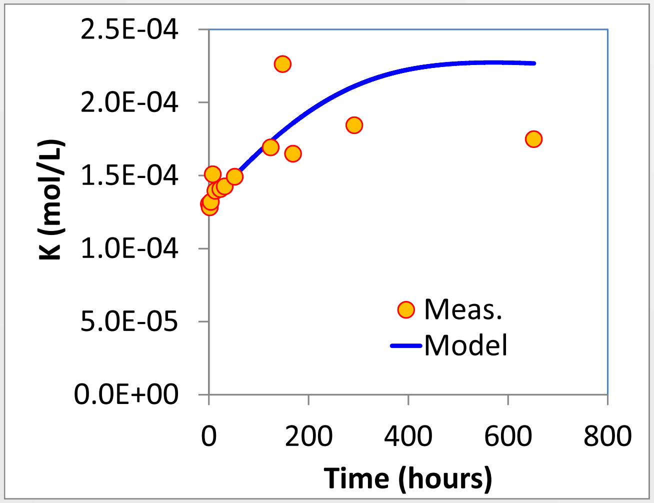
Carbonates dissolution





Silicates dissolution



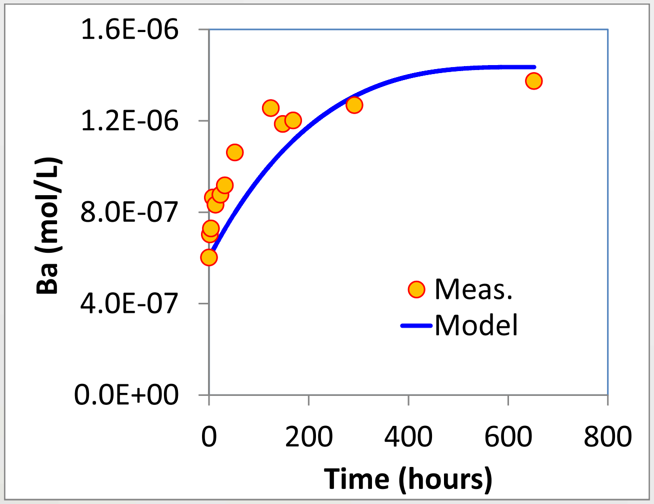


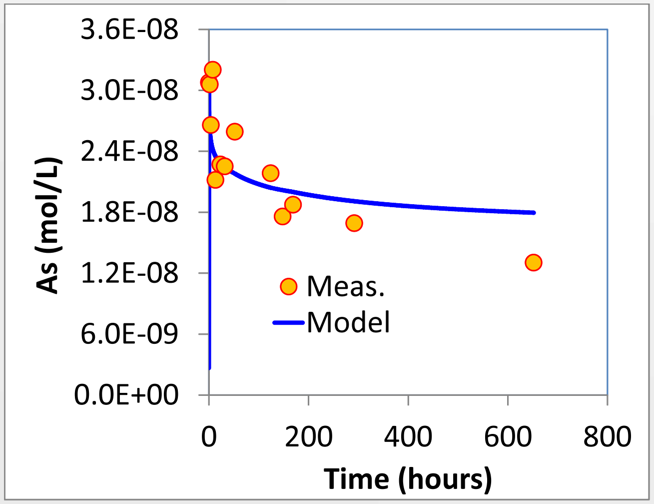
Laboratory batch experiments of water-rock-CO_2 interactions

Results

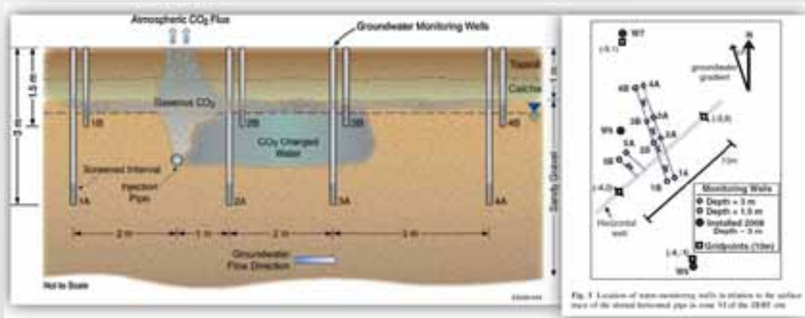
Mobilization of trace metals dominated by two mechanisms

- Carbonate dissolution, such as Ba, Mn, Sr
- Desorption/adsorption, such as As, Pb

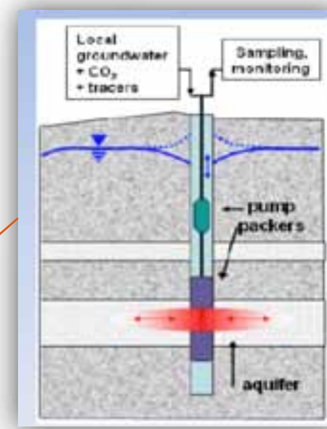




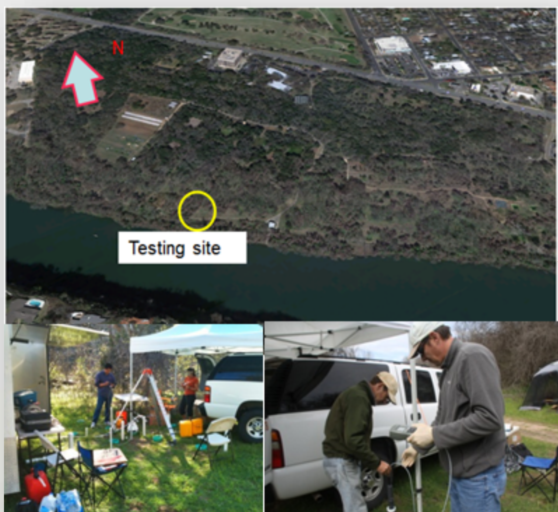
Field controlled-release experiments



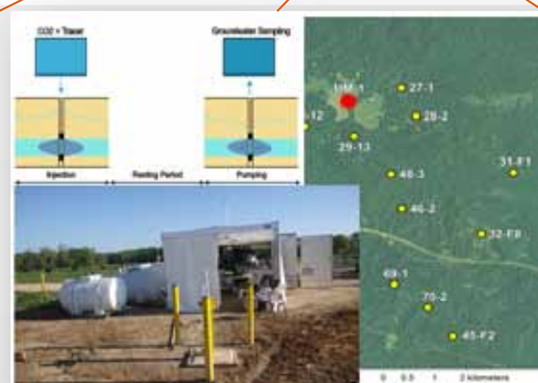
Kharaka et al. (2010)
Zheng et al. (2012)



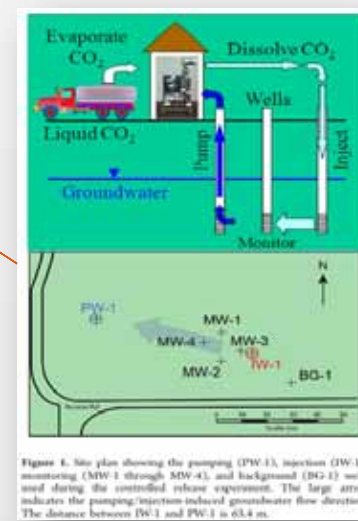
Q. Yang et al. (2013), Newark Basin



Mickler et al. (in preparation),
Yang et al. (in preparation)



Yang et al. (2013)

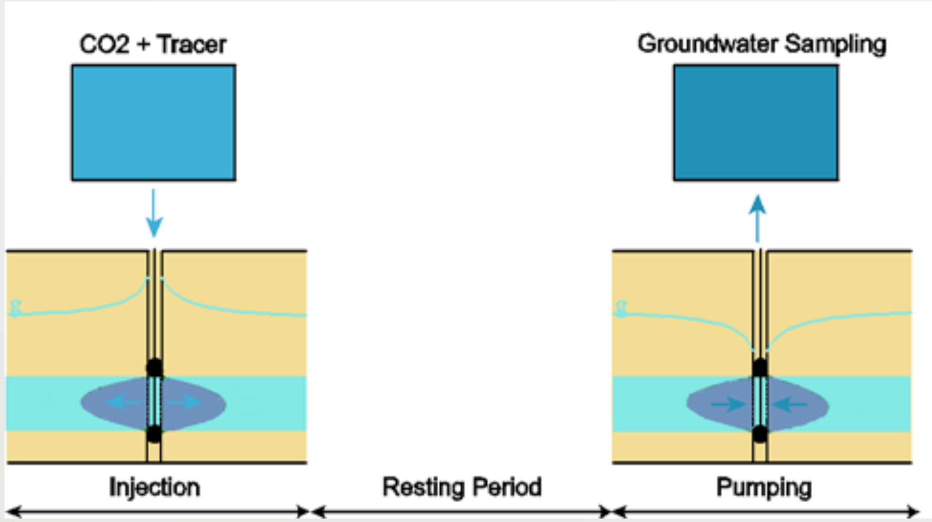


Trautz et al. (2012, 2013)

Field controlled-release experiments

Single well push-pull test

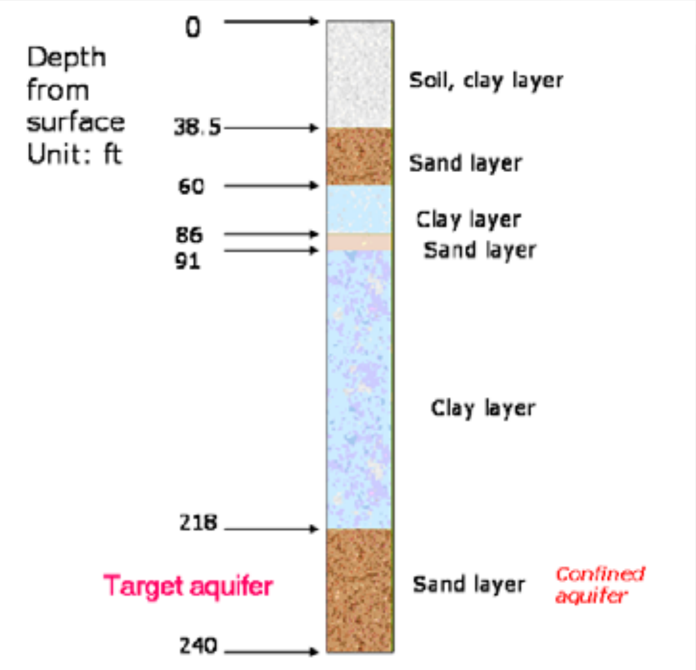
- The injection phase: inject groundwater saturated with CO_2 into the target aquifer
- The resting phase: let injected water react with aquifer sediments
- The pulling phase: pump groundwater continuously for collecting water samples



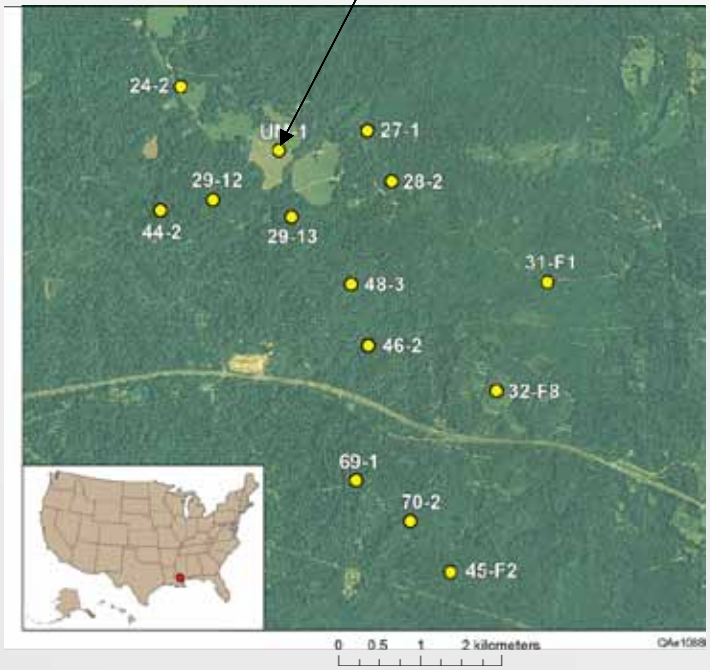
Field controlled-release experiments

Single well push-pull test

- The well was drilled in Nov. 2008
- The well was completed with 2” PVC and screened at the 180 to 240 ft
- Depth of the well: 240 ft to surface
- Depth of water level: 90 ft to surface



Testing well

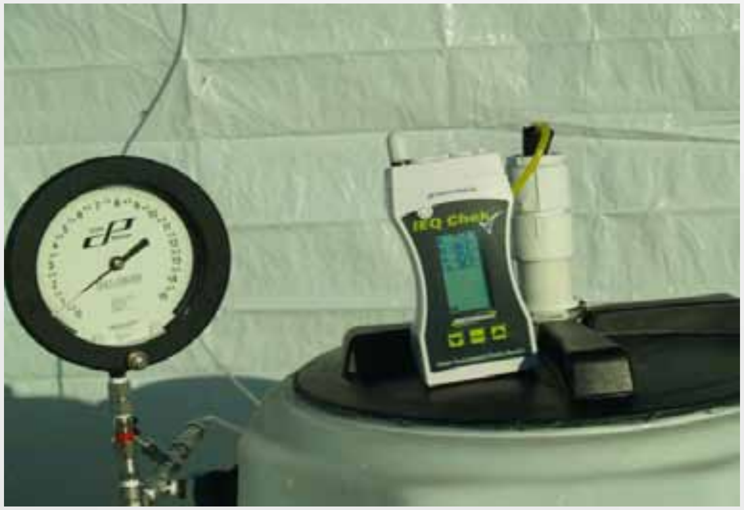


Field controlled-release experiments

Single well push-pull test

Field controlled-release experiments

Single well push-pull test



Field controlled-release experiments

Single well push-pull test

- ✓ The injection phase:
  Injection started at ~7:00 pm, March 23
  Total 3825 L water injected during 8 hours
- ✓ The resting phase:
  ~55 hours
- ✓ The pulling phase:
  Pumping started at ~9:10 am, March 26
  ~15142 L groundwater pumped out during ~11 hours

Onsite measurements

- ✓ pH, alkalinity
  conductivity
  temperature

Water samples

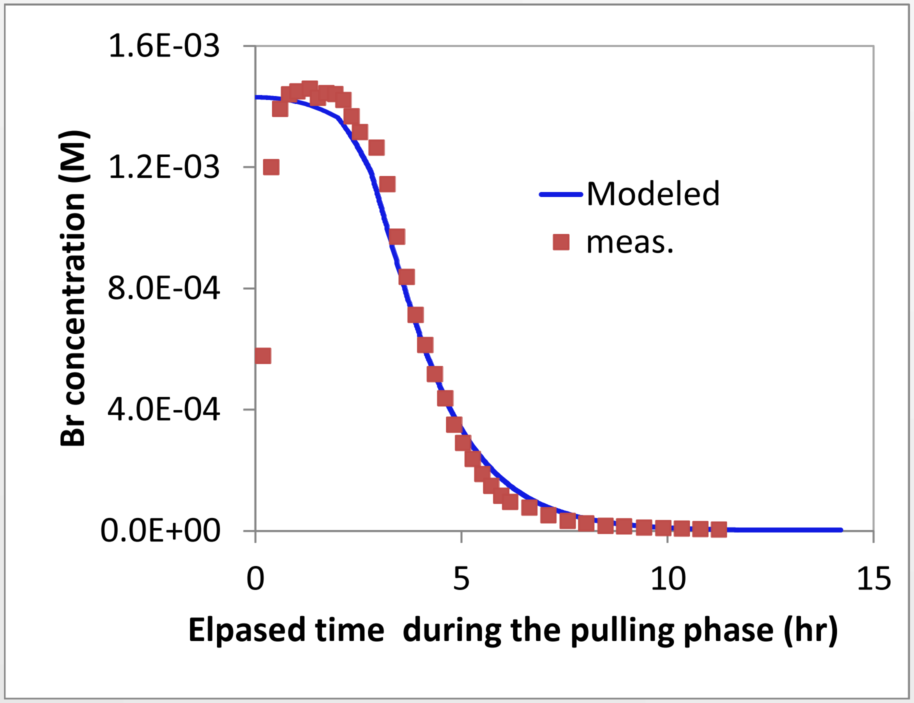
- ✓ IC analysis
- ✓ ICP-MS analysis
- ✓ DIC and stable carbon isotope of DIC

Field controlled-release experiments

Single well push-pull test

Results

- Breakthrough of Br   inj.: 1.43 mmol/l, bkg: ~0

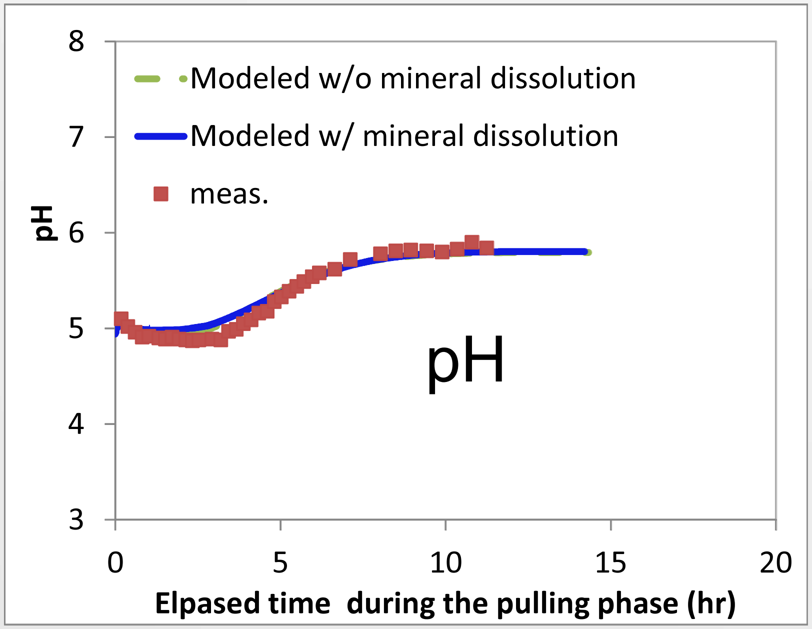


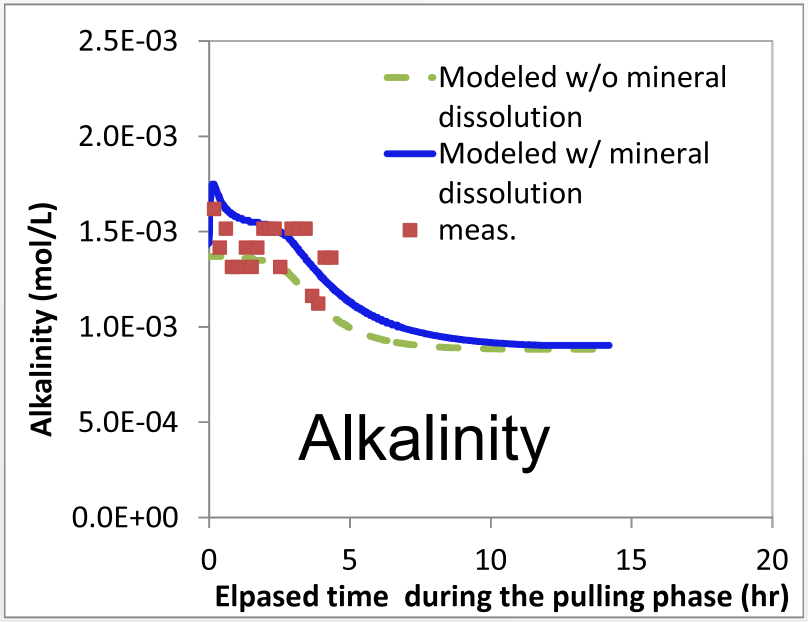
Changbing Yang, Pat Mickler, Robert Reedy, Bridget R. Scanlon, Katherine D. Romanak, J.P. Nicot, Susan D. Hovorka, Ramon Trevino, Toti Larson, Single-Well Push-Pull Test for Assessing Potential Impacts of CO2 Leakage on Groundwater Quality in a Shallow Gulf Coast aquifer in Cranfield, Mississippi, International Journal of Greenhouse Gas Control, in press.

Field controlled-release experiments

Single well push-pull test

Results



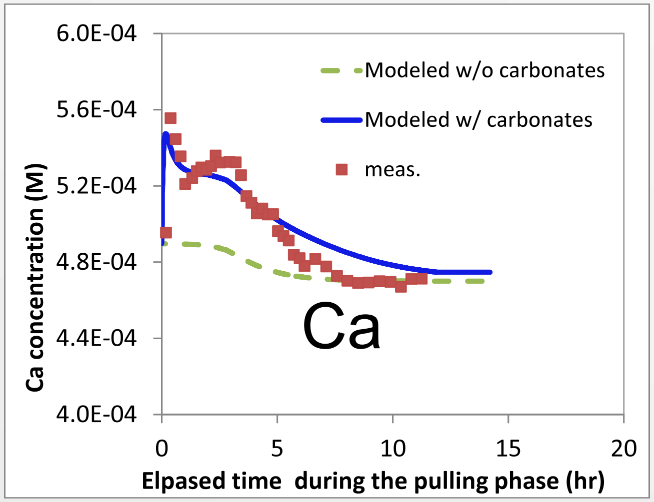


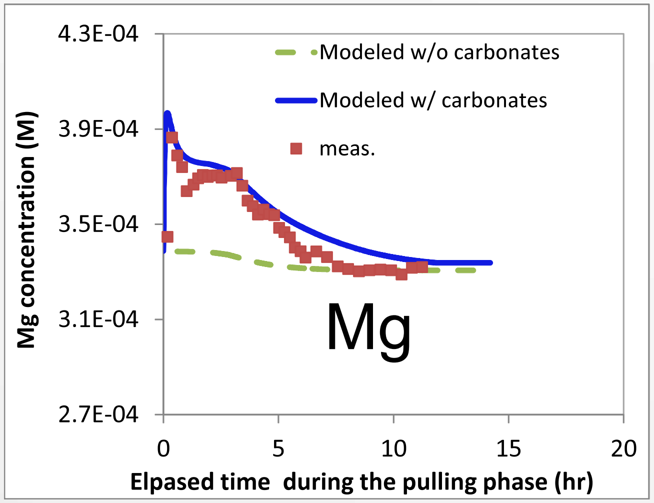
Field controlled-release experiments

Results

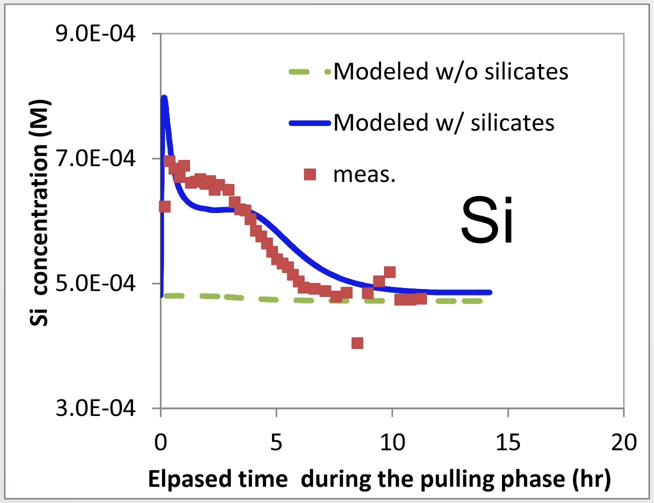
Single well push-pull test

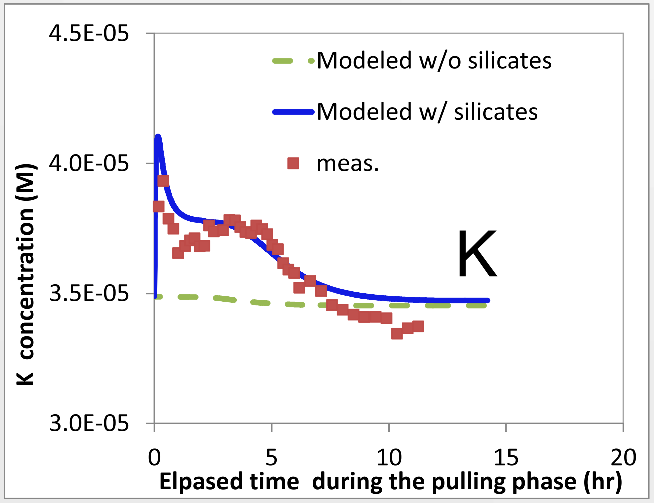
- Carbonate dissolution





- Dissolution of silicates



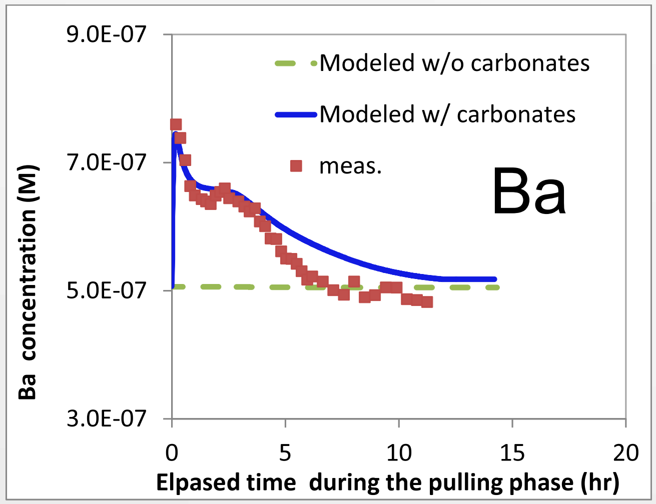


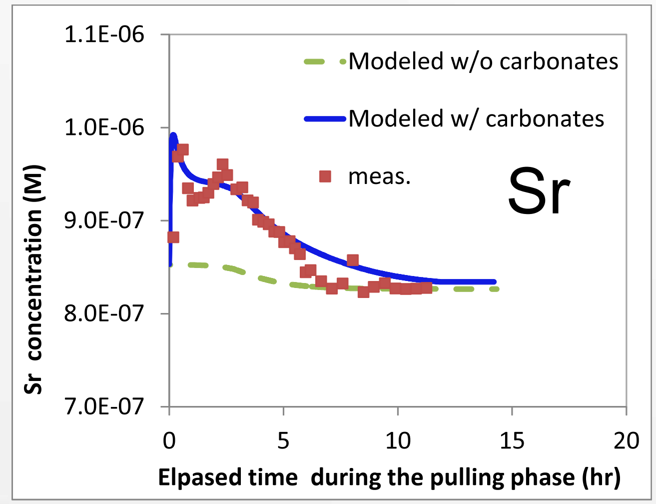
Field controlled-release experiments

Single well push-pull test

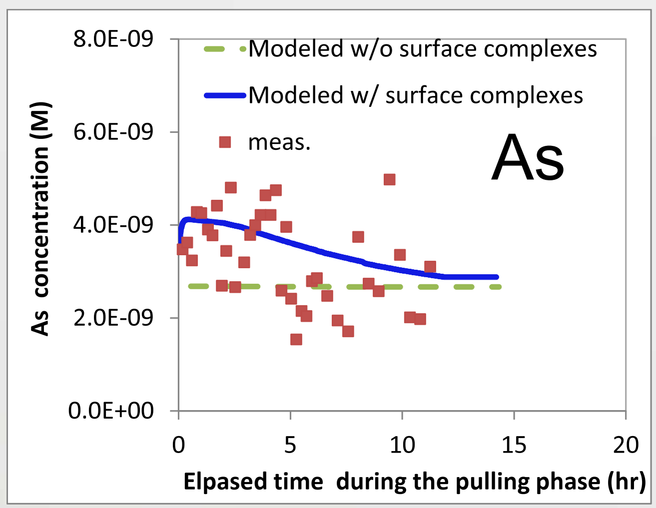
Mobilization of trace metals

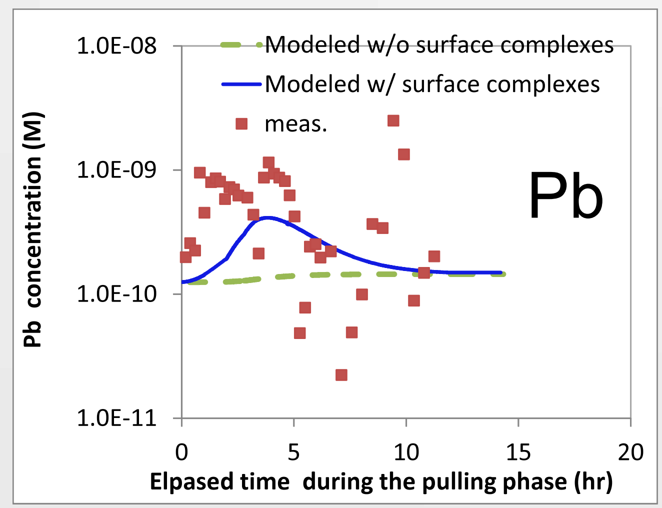
- Carbonate dissolution





- Adsorption/ desorption





Field controlled-release experiments

Comparison of maximum concentrations observed in push-pull test with concentration measurements from 14 wells at Cranfield shallow aquifer

Ions	Unit	Max Conc.	Statistics of concentration measurements	
			Min	Max
pH	-	5.0	5.3	7.5
Alkalinity	mg $CaCO_3$/L	80.9	30.0	154.3
DIC[8]	mmol/L C	35.25	1.3	5.5
Ca	mg/L	22.3	4.0	27.9
Mg	mg/L	9.4	1.6	10.2
K	mg/L	1.5	1.1	8.4
Na	mg/L	-	7.6	74.3
Si	mg/L	19.5	1.9	23.0
Ba	µg/L	104.3	10.0	258.0
Cu	µg/L	0.9	<3.0	34.0
Fe	mg/L	0.2	<0.007	11.2
Mn	µg/L	13.4	1.0	708.0
Zn	µg/L	20.2	3.0	1187.0

Summary

- Groundwater chemistry at the Cranfield shallow aquifer appears to be dominated by silicate mineral weathering;
- Batch experiments, the field controlled-release test, and numerical modeling show that DIC and pH are sensitive to CO_2 leakage and may be used for detecting CO_2 leakage at the Cranfield shallow aquifer;
- Dominant geochemical processes for ion mobilization include dissolution of carbonates and silicates, desorption/adsorption;
- No obvious degradation in groundwater quality was observed in the batch experiments and the field test;

Summary

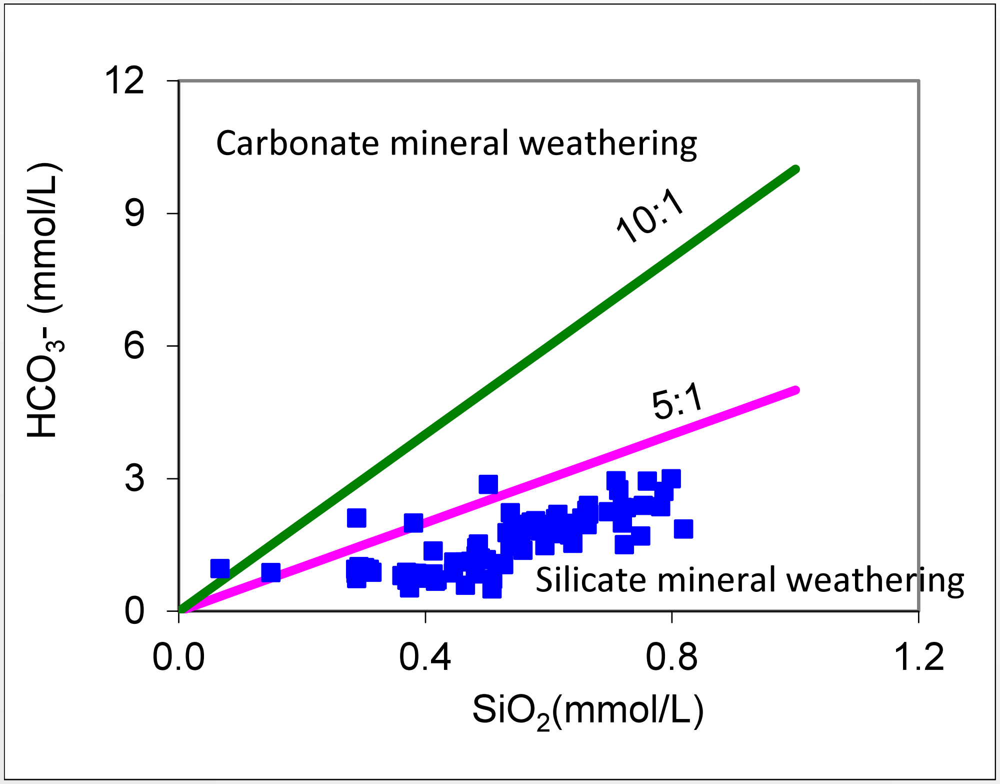
- Maximum concentrations of trace metals observed, such as As and Pb, are much less than the EPA contamination levels;
- Single well push-pull test appears to be a convenient field controlled-release test for assessing potential impacts of CO_2 leakage on drinking groundwater resources;
- Stepwise monitoring strategy used for groundwater study at the Cranfield site may be applied to other sites;
- The combined use of laboratory batch experiments, field controlled-release tests, and reactive transport models provide a comprehensive evaluation of potential impacts of CO_2 leakage on groundwater chemistry.

Supplementary slides

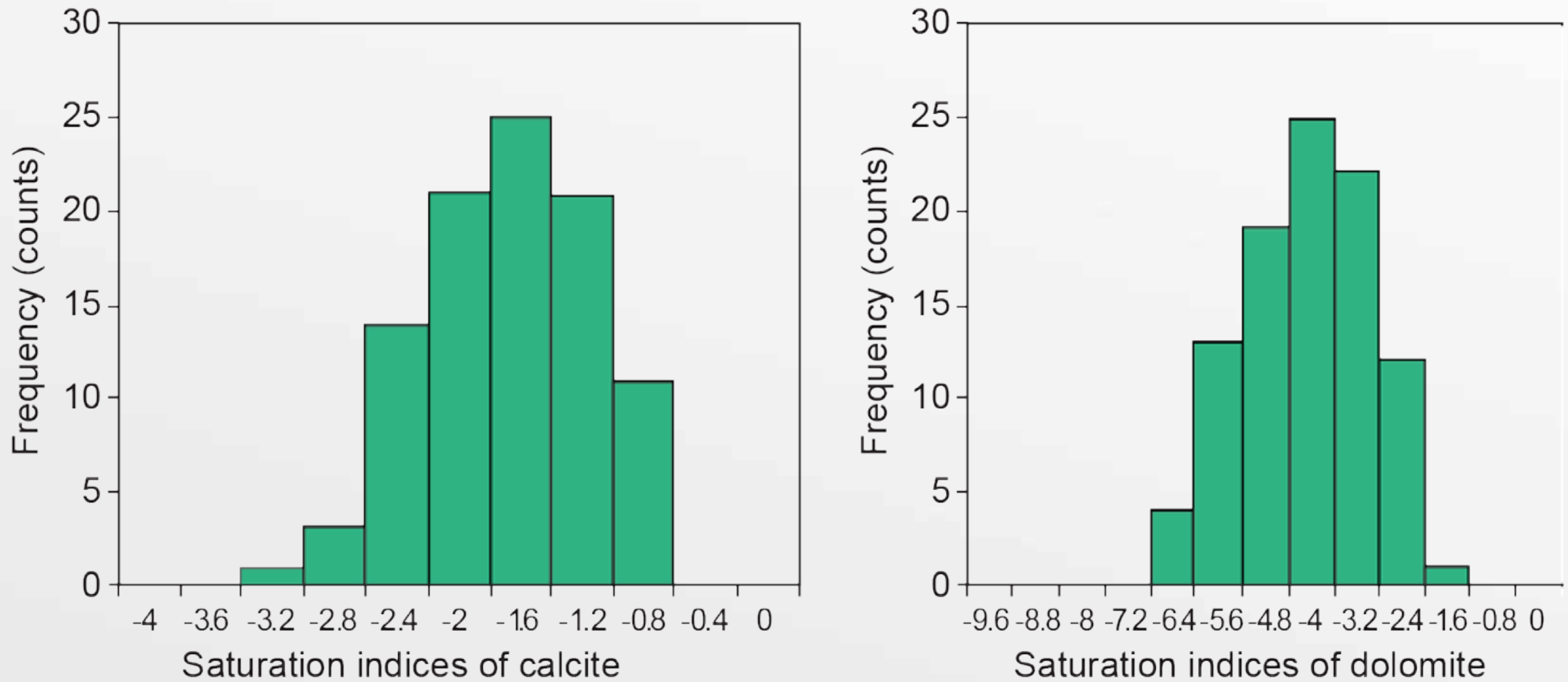
Characterization of Groundwater Geochemistry (3/6)

- $HCO_3/Si>10$: water chemistry is dominated by carbonate mineral weathering
- $HCO_3/Si<5$: water chemistry is dominated by silicate mineral weathering

Hounslow, A. 1995. Water Quality Data: Analysis and Interpretation. New York, New York: Lewis Publishers.



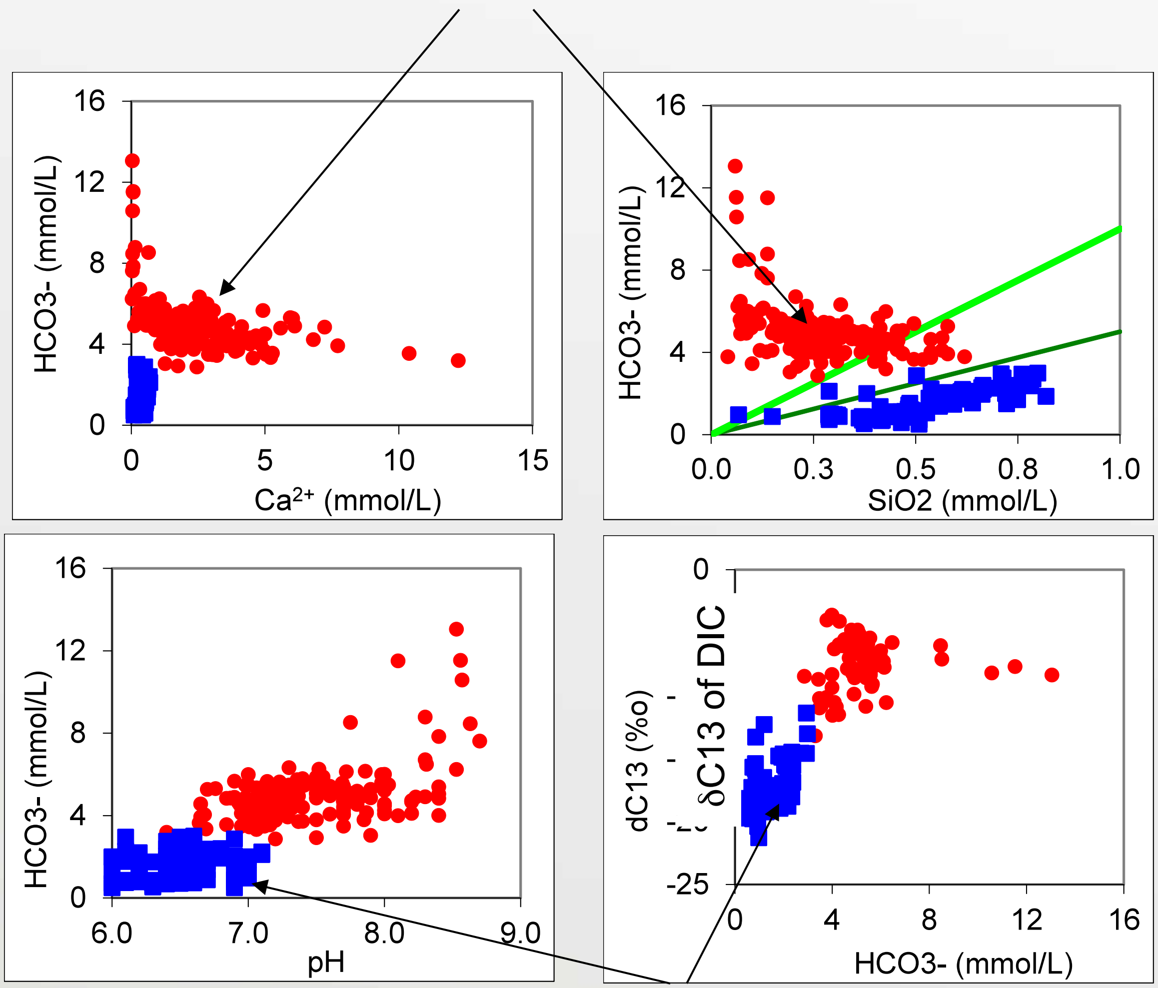
Characterization of Groundwater Geochemistry (4/6)



- Carbonate mineral saturation indices show that carbonate minerals (calcite and dolomite) are under saturated with respect to groundwater

Characterization of Groundwater Geochemistry (6/6)

SACROC



Cranfield

SACROC aquifer sediments contain carbonate minerals

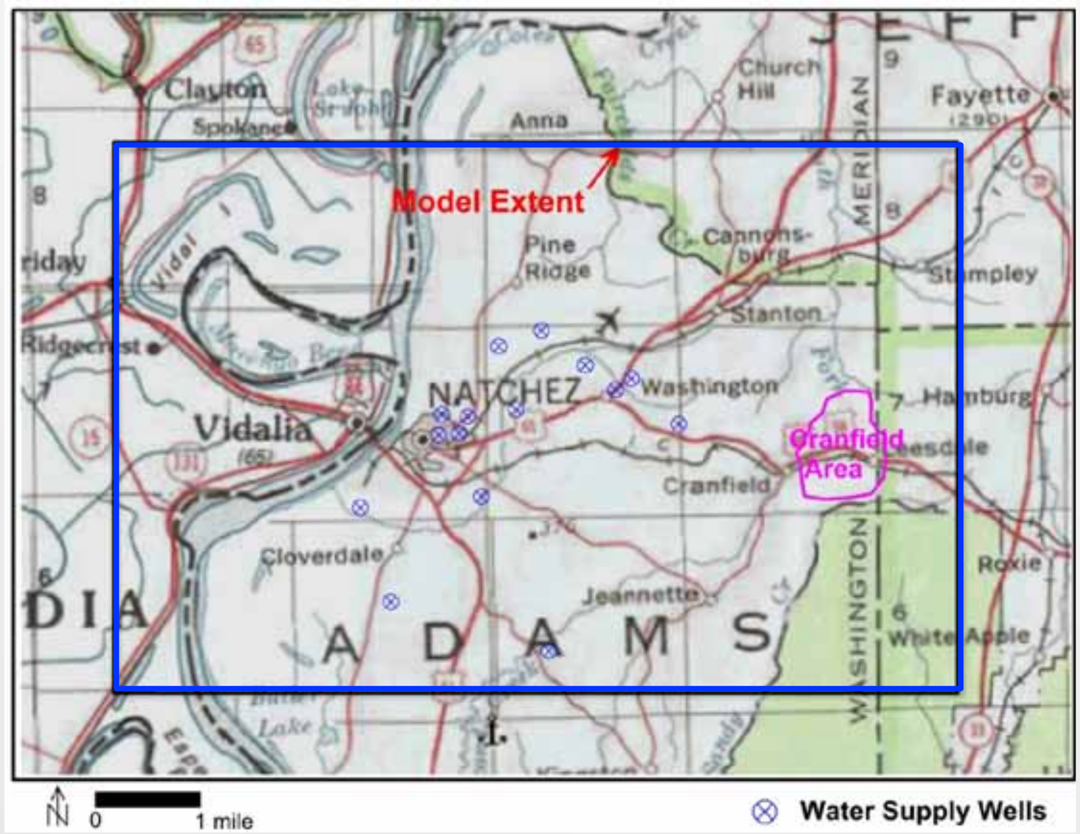
Cranfield aquifer sediments without carbonate minerals

Numerical Modeling

- Regional scale
- Fixed head boundary based on USGS water level data
- Production at pumping wells based on USGS data
- Worst scenarios for CO_2 leak
- Model tool: MODFLOW, MT3D, PHREEQC

Reactive transport modeling

By Anchor QEA



Geochemical processes if CO_2 has leaked into a shallow aquifer

- CO_2 dissolution into groundwater

  $CO_2 + H_2O \rightarrow H_2CO_3$ $H_2CO_3 \rightarrow H^+ + HCO_3^-$ $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

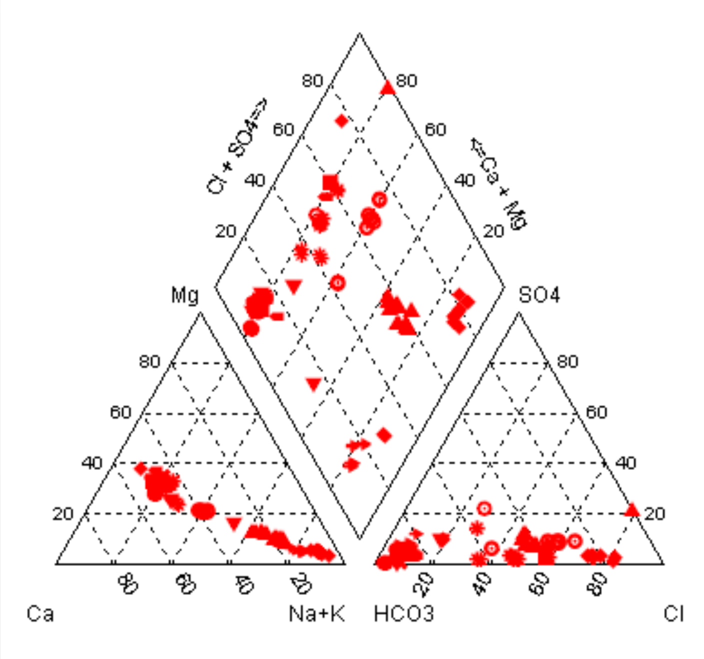
- Mineral dissolution

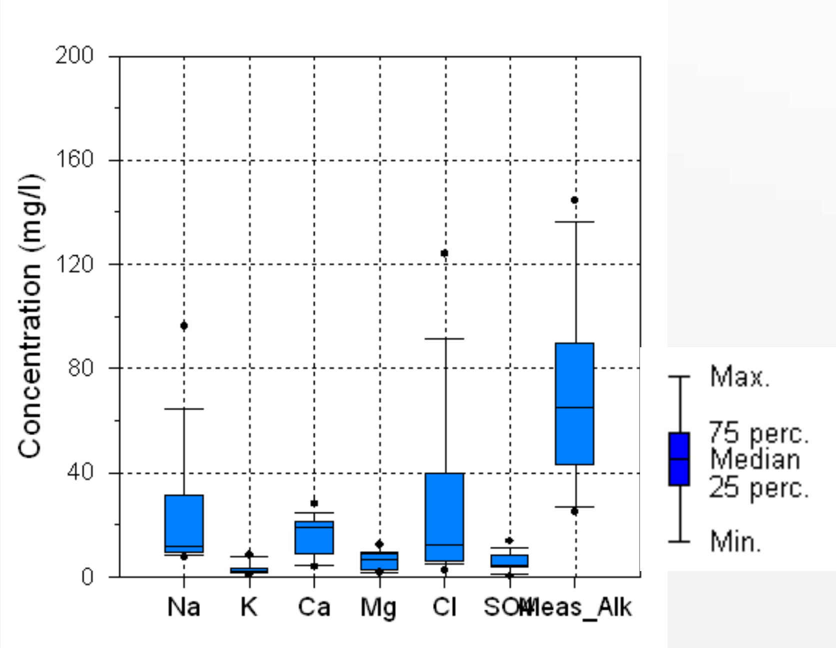
  $H_2O + CaCO_3 + CO_2 \rightarrow 2HCO_3^- + Ca^{2+}$

- Mobilization of trace metals (Fe, Mn, Pb, Zn, U, As, Cd, Sr,…)

- Redox (oxidation-reduction)

Characterization of Groundwater Geochemistry





- Groundwater types mainly are Na-Cl, Ca-Na-HCO3, and Ca-Na-HCO3-Cl
- Na and Cl concentrations show variations

Maximum concentrations of trace elements observed at Cranfield shallow aquifer (as of March 2012)

Trace metals	Ba	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Maximum concentration (ppm)	0.258	0.004	0.003	0.034	11.17	0.71	0.065	1.19

Characterization of Groundwater Geochemistry

- Calculated saturation indices of calcite and dolomite are under saturated with respect to groundwater
- Ratios of HCO_3/Si < than 10
- $\delta^{13}C$ of DIC ranges from -14‰ to -26‰

Mineral compositions of aquifer sediment

Depth (m)	Quartz	Microcline	Illite	Kaolinite	Albite
61.26	38.76	17.5	19.74	20.85	3.15
67.97	81.86	9.26	1.64	5	2.24
69.49	59.35	17.27	2.79	18.16	2.43
70.10	32.84	18.46	14.39	32.96	1.35
71.02	50.93	20.91	5.31	21.76	1.09

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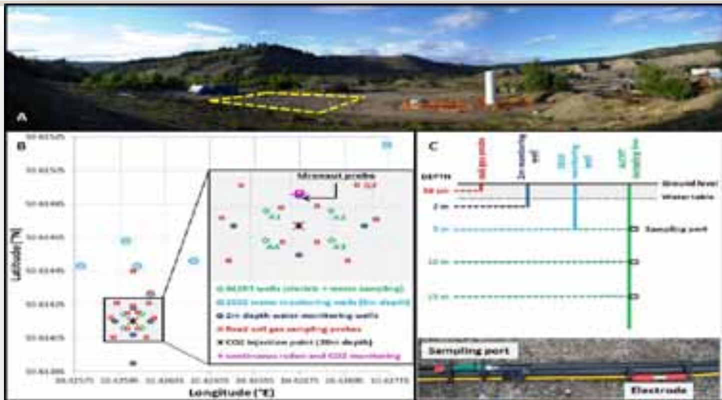
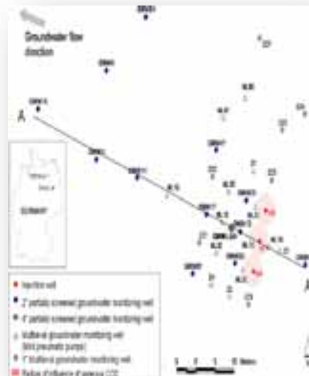


Gal et al. (2013)

- Fluvial-glacial deposits;
- Gaseous CO_2 injected for ~6 days at the interval ~20 m;
- Groundwater samples at different depths, in-situ continuous monitoring.

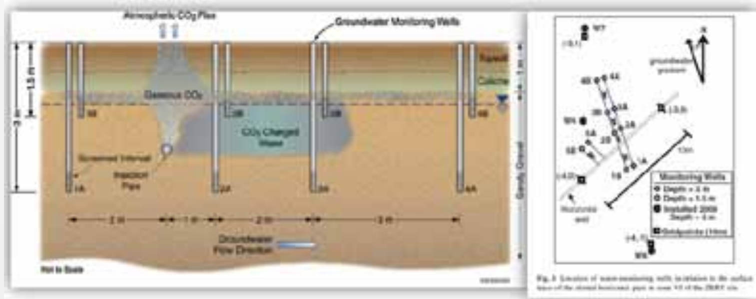
- Major findings:
  Injection of CO_2 induced pH/alk changes and also chemical variations both in time and space; Even well-characterized, natural deposits makes identification of CO_2 leakage challenging.



Peter et al. (2012)

- Medium to course sand, silt;
- Gaseous CO_2 injection into three wells for ~10 days at the interval ~18 m;
- Groundwater samples at different depths, geo-electrical measurements, multi-parameter probes.

- Major findings:
  DIC (Dissolved Inorganic Carbon) increased and pH decreases due to CO_2 injection; Release of major cations and trace elements was observed; Lab DIC measurements are less reliable than values obtained by multiparameter probes or by field titration and pH measurements



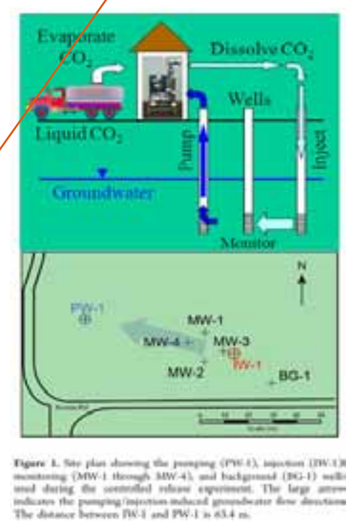
Kharaka et al. (2010), Zheng et al. (2012)

- Injection interval: 2-3 m;
- Sandy gravel;
- Gaseous CO_2 through horizontal pipe for ~ 1 month;
- Onsite pH, Eh, EC, T; groundwater samples for major ions & trace elements, DOC, BTEX;
- Major findings:

  pH, alkalinity, and EC show systematic change;

  Major ions and some trace elements show obvious increase in concentration;

  Pb and As show very minor increase which may be related to exchange reactions.



Trautz et al. (2012, 2013)

- Injection interval: 47-55m;
- Gray-green fine grained silty sand;
- Groundwater saturated with CO_2 for ~5 months;
- Groundwater samples, in-situ logging, complexly spaced electrical methods.

- Major findings:

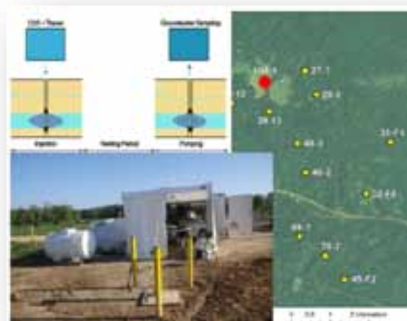
  pH shows 3 unit drops;

  As and Pb are below detection limit;

  Some ions (Ba, Ca, Cr, Sr, Mg, Mn, Fe) show a pulse response.

Mickler et al. (2012), Yang et al. (2013)

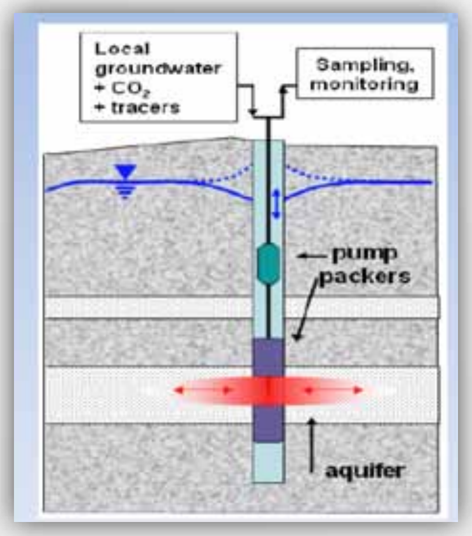
- Injection interval: 2.5-6 m;
- Fine, silty sand with abundant carbonates;
- Groundwater saturated with CO_2, injection for ~ 1 hr;
- Onsite pH, Eh, EC, T, Alk, Groundwater samples for major ions & trace elements.
- Major findings:
  Lower pH leads to carbonates dissolution;
  Trace elements were mobilized from aquifer materials, however, lower than EPA MCLs;
  Increases in Ca & alkalinity are significant.



Yang et al. (2013)

- Injection interval: 66-73 m;
- Fine sand, silty sand;
- Groundwater saturated with CO_2 injection for ~8 hrs;
- Onsite, pH, Eh, EC, T, Alk; Groundwater samples.
- Major findings:
  Conc. of major ions elevated during mineral dissolutions; moblization of some trace elements come from carbonates dissolution; As and Pb show minor increases but much smaller than EPA MCLs; Dissolution of small amount of carbonates may be significant to mobilization of trace elements

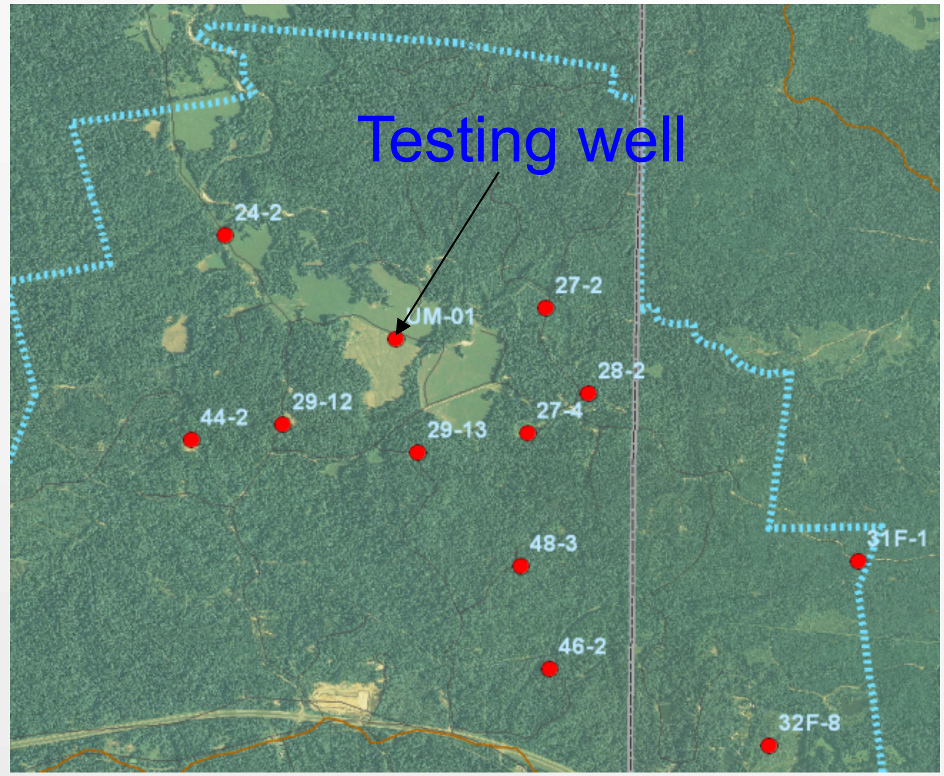
- Field Tests (Single well)

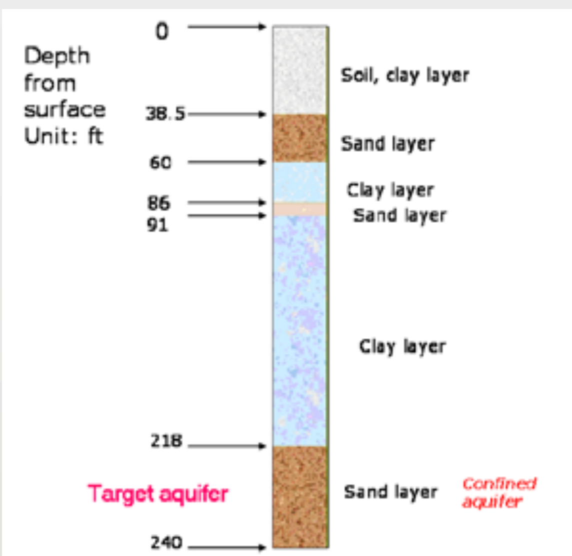


Q. Yang et al. (2013), Newark Basin, US

- Injection interval: 362-366 m;
- Fractured sandstone;
- Groundwater saturated with CO_2, injection for ~ 10 hr;
- Onsite pH, Eh, EC, T, Alk; Groundwater sampled for major ions & trace elements.
- Major conclusions:
  Lower pH causes mobilization of trace elements.

- The well was drilled in Nov. 2008
- The well was completed with 2” PVC and screened at the 180 to 240 ft
- Depth of the well: 240 ft to surface
- Depth of water level: 90 ft to surface





Mineral compositions of aquifer sediment

Depth (m)	Quartz	Microcline	Illite	Kaolinite	Albite
61.26	38.76	17.5	19.74	20.85	3.15
67.97	81.86	9.26	1.64	5	2.24
69.49	59.35	17.27	2.79	18.16	2.43
70.10	32.84	18.46	14.39	32.96	1.35
71.02	50.93	20.91	5.31	21.76	1.09