# Geochemical characterization of shallow groundwater at the Cranfield aquifer and numerical simulation: Can pH and carbonate parameters be used to detect potential $CO_2$ leakage at geological $CO_2$ sequestration sites?

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Gulf Coast Carbon Center


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# Geochemical characterization of shallow groundwater at the Cranfield aquifer and numerical simulation: can pH and carbonate parameters be used to detect potential $CO_2$ leakage at geological $CO_2$ sequestration sites?

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The Gulf Coast Carbon Center (GCCC) is currently studying $CO_2$ sequestration at Cranfield, Mississippi. One study focuses on whether groundwater monitoring can provide information for detecting potential $CO_2$ leaks through preferential flow paths, such as historic production wells. Water well geophysical logging at the Cranfield site suggests that a sand layer (200-300-ft-depth) accommodates a major freshwater aquifer which has been sampled quarterly to characterize baseline groundwater chemistry.
The Cranfield shallow aquifer is mainly Na-Ca-Mg-$HCO_3$-Cl and is under saturated with respect to calcite (SI = -0.5 to -2.5) and dolomite (SI = -1.1 to -4.8). This result is consistent with SEM and XRD petrographic analysis of aquifer sediments that contain mainly silicate and clay minerals without carbonate. $\delta^{13}C$ of groundwater ranges from -26. to -15 ‰, indicating possible dissolution of microbial $CO_2$. Geochemical models considering silicate mineral dissolution under different scenarios of $CO_2$ input indicate that pH will decrease and DIC will increase with increasing $CO_2$ pressure, which may build up in the confined aquifer in the event of a CO2 leak. Values of $\delta^{13}C$ of $CO_2$ currently injected at Cranfield (-2.6 to -4.7‰) are significantly heavier than values for background DIC in groundwater, therefore both pH and carbonate parameters (DIC of groundwater and $\delta^{13}C$) could be indicators for detecting $CO_2$ leakage in the Cranfield aquifer. This conclusion, however, is in contrast with another study conducted in west Texas where carbonate parameters were found not to be effective indicators due to the dissolution of dolomite in the aquifer.

# Ninth Annual Conference on Carbon Capture & Sequestration

*Innovative Sequestration Systems*

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# SECARB III

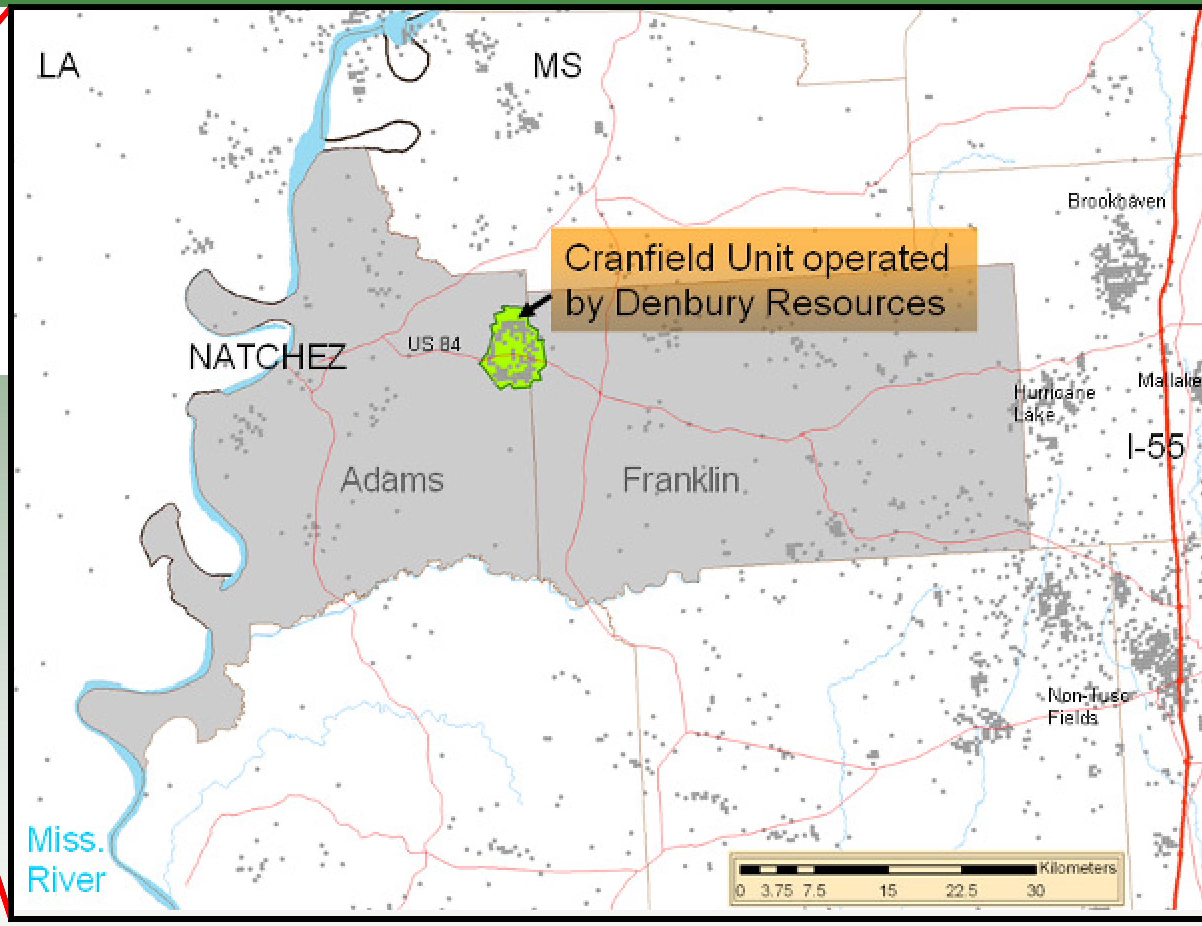
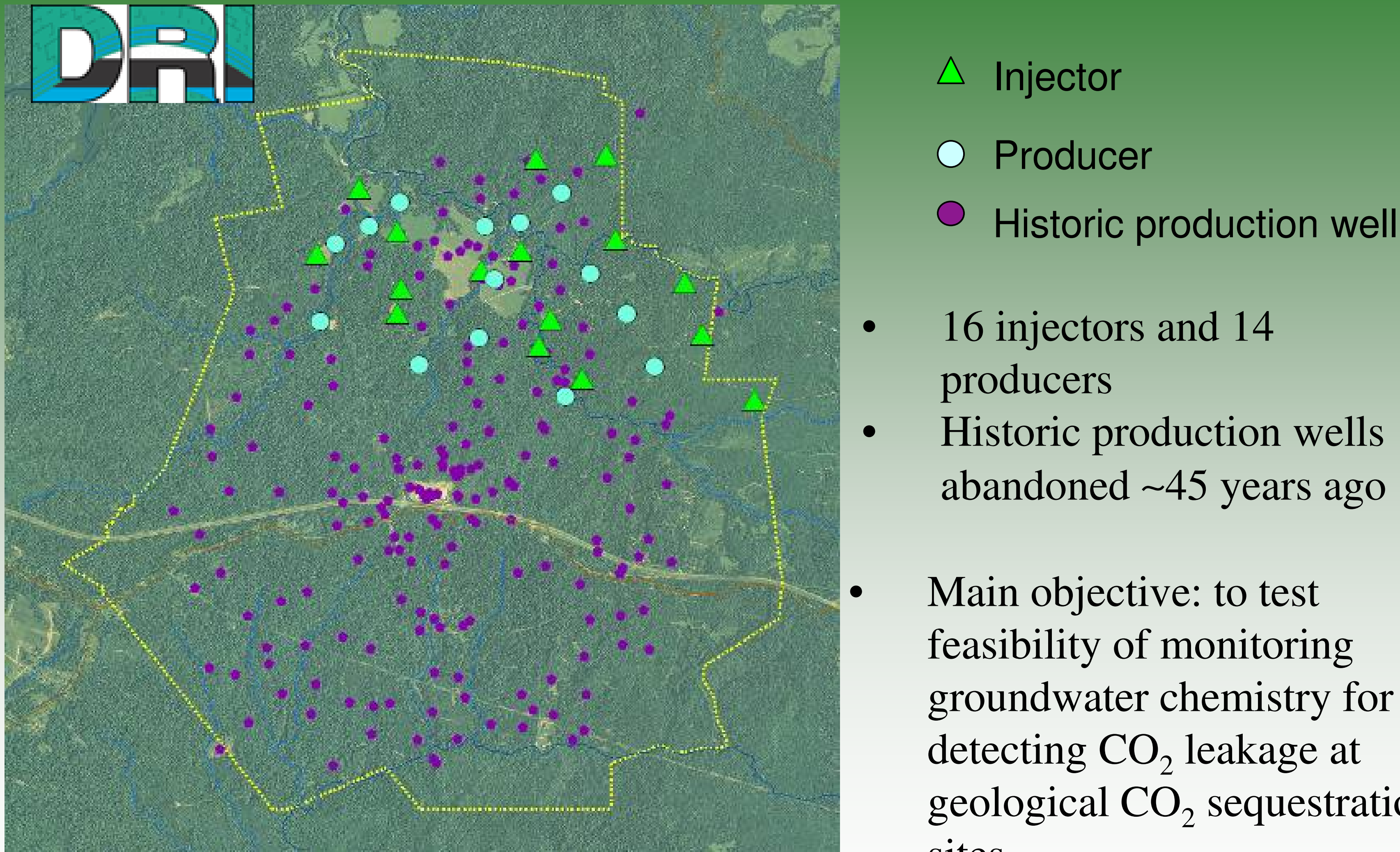




Figure courtesy of Tip Meckel

- Located 15 miles east of Natchez, MS
- Owned and operated by Denbury Resources
- Injection of $CO_2$ for EOR since 2008

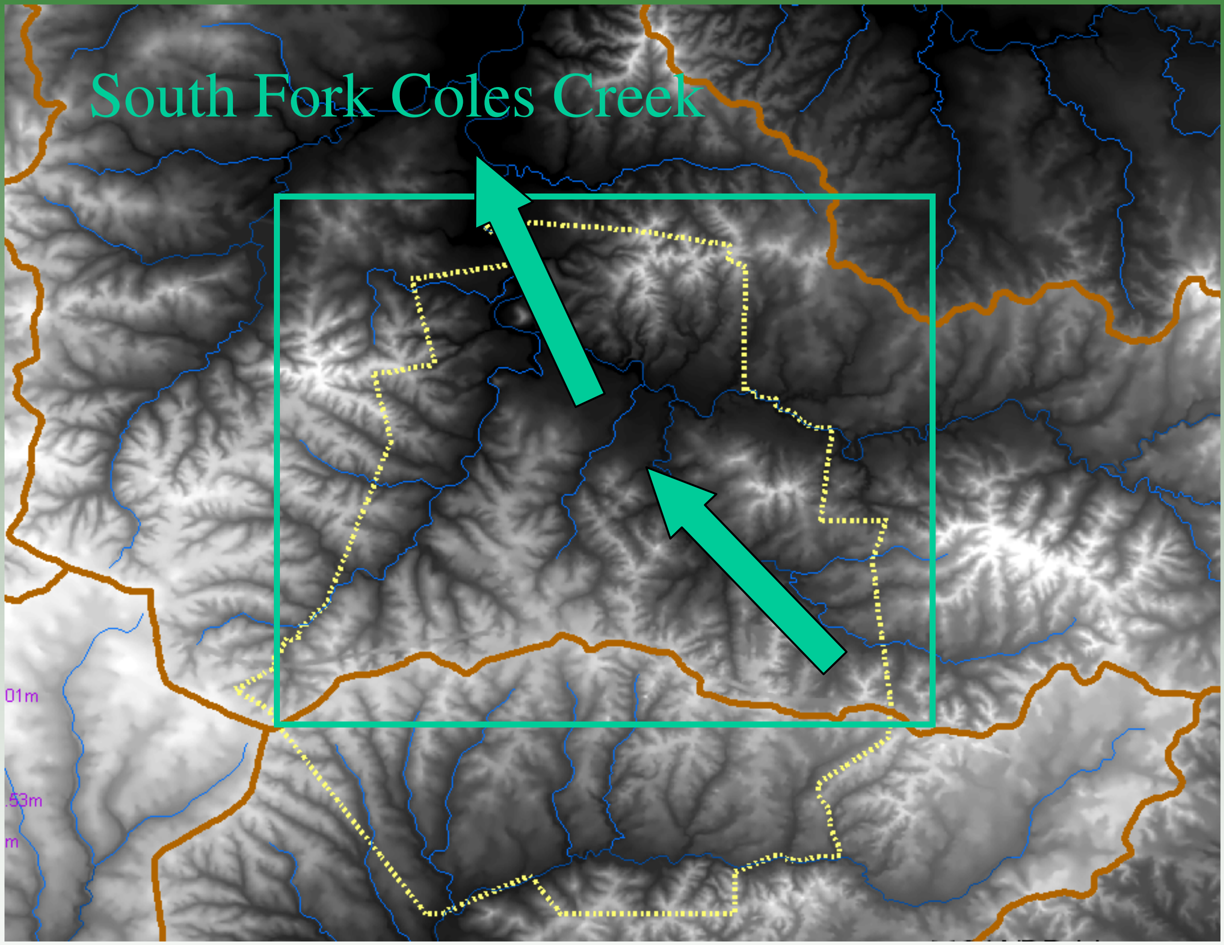
# Injection of $CO_2$ at the Cranfield




- 16 injectors and 14 producers
- Historic production wells abandoned ~45 years ago

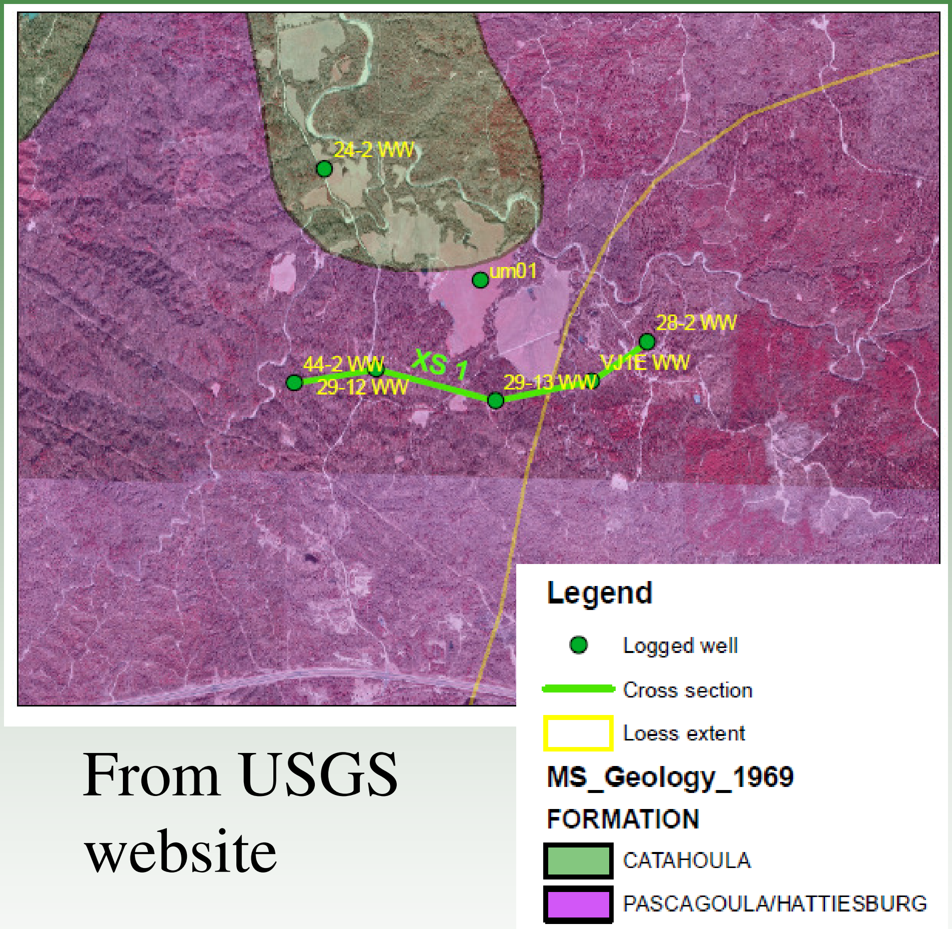
- Main objective: to test feasibility of monitoring groundwater chemistry for detecting $CO_2$ leakage at geological $CO_2$ sequestration sites

# Hydrology




- Average annual precipitation is about 54 in.
- Monthly precipitation from 1.65 in. in Oct. to 6.13 in. in March
- Mean annual air temperature: 66 °F (19 °C)
- Mississippi River is 15 miles to the west
- Surface runoff from southeast to northwest
- Heavily wooded and hilly

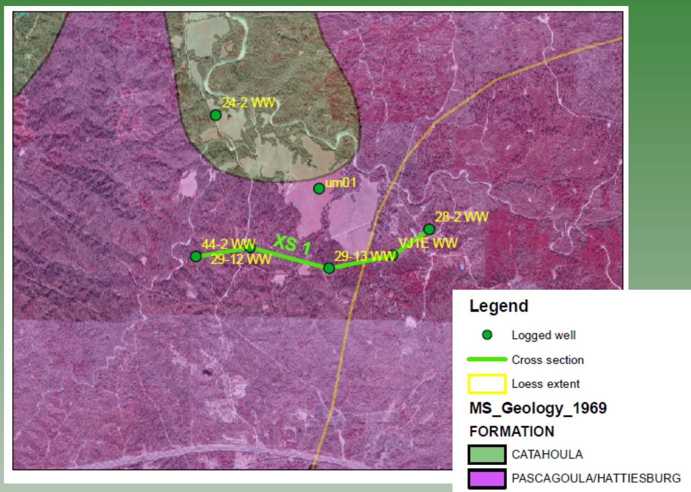
# Geology




From USGS website

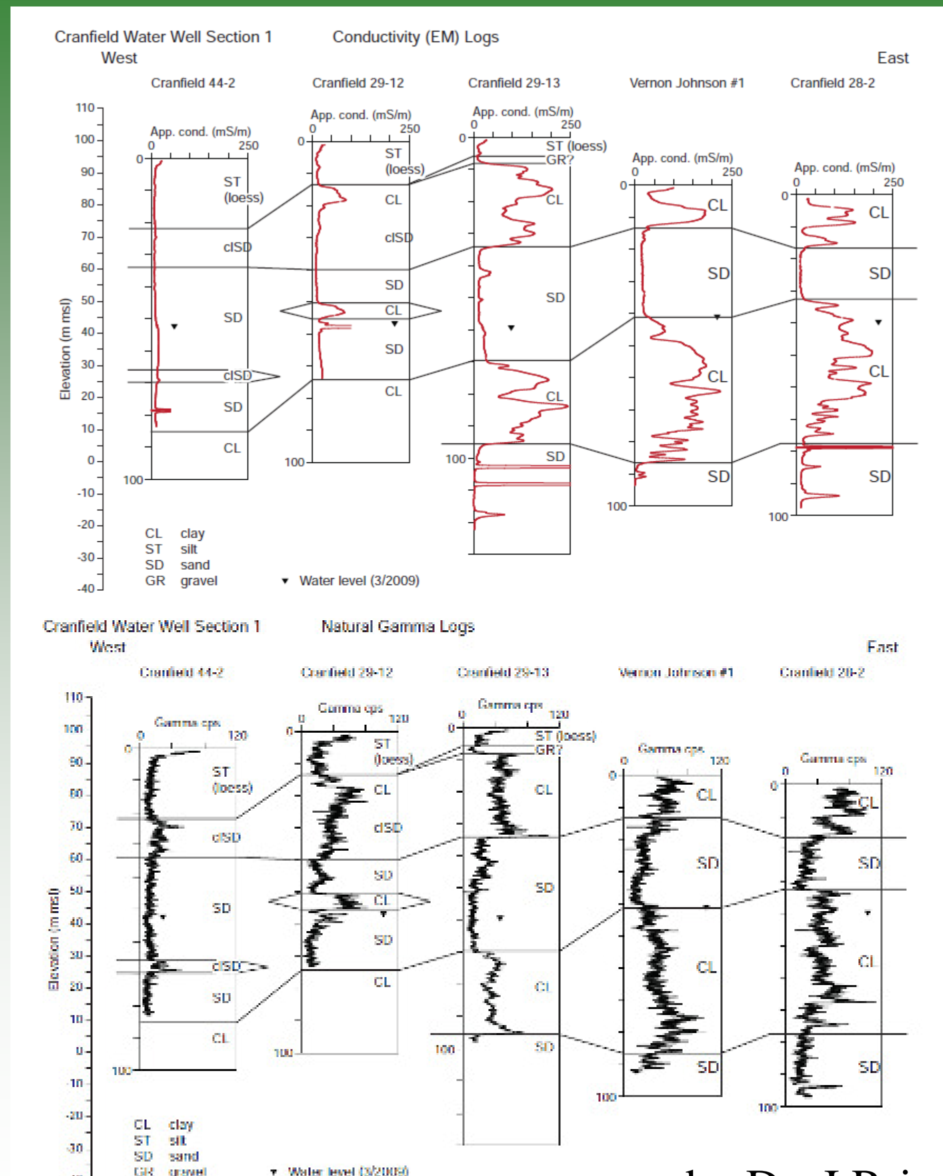
- Catahoula formation at the northwest of the area
  Features: Irregularly bedded gray sand and sandstone
- Pascagoula/Hattiesburg formation
  Features: Green and bluish-green clay, sandy clay, and sand; gray siltstone and sand
- Thickness of Loess decreases from west to east

# Geophysical logging



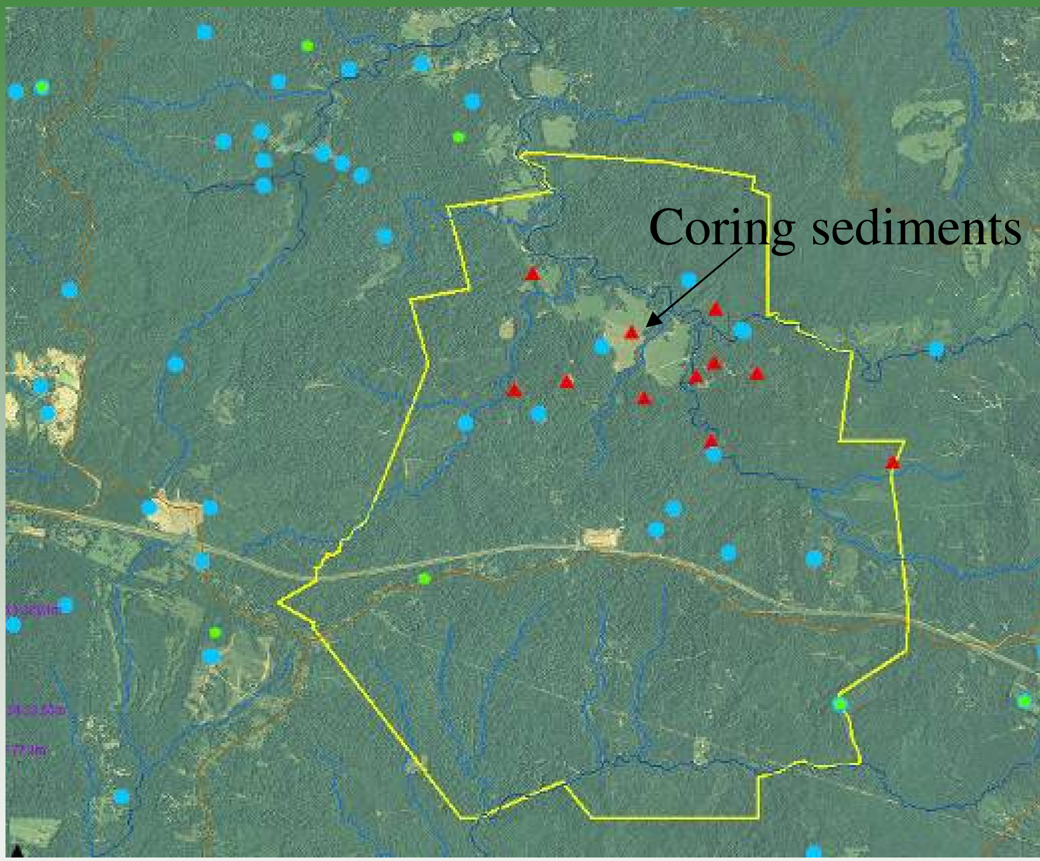

- Logging 7 water wells for conductivity and natural gamma
- Sand layers at depths from 30 to 100 meters below surface
- Sand layers become thicker from east to west
- Clay layers are thick

Coastal lowlands aquifer system in national aquifer




by Dr. J Paine

# Groundwater wells



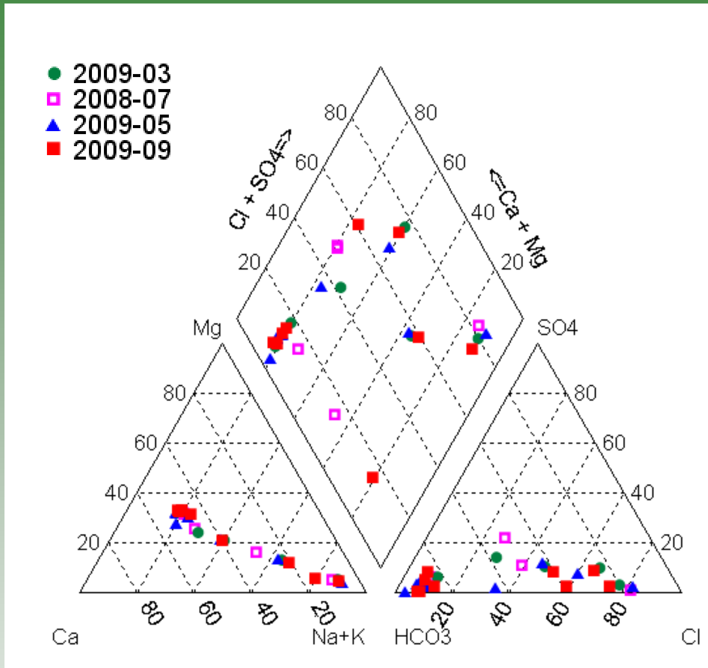

- “makeup” water well
- Water wells surveyed by USGS
- Private well

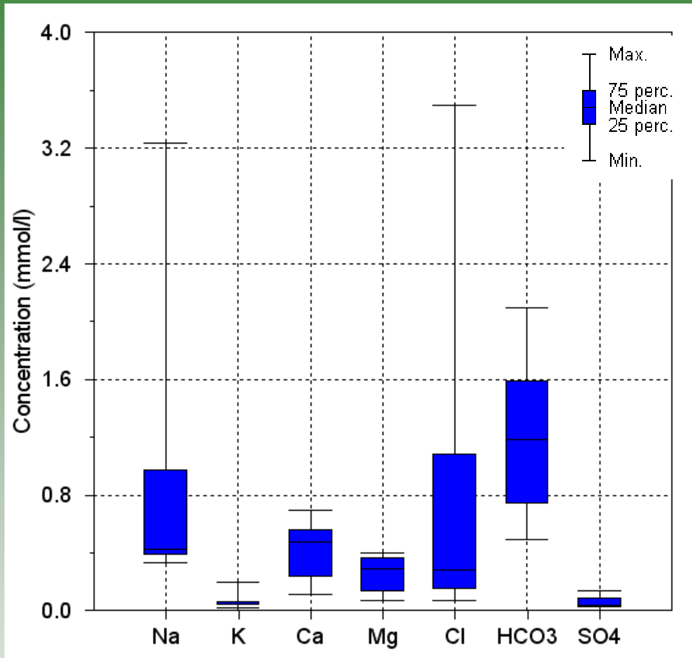
- Groundwater mainly for domestic water supply
- Some “makeup” water wells drilled in last several years for oil well drilling, water production ranges from 150 to 380 liters per minute
- USGS surveyed groundwater wells in past 30 years for water levels
- A well with a depth of 73 meters drilled for coring sediments

# Groundwater sampling and geochemical analysis

- Four field trips for groundwater sampling since August, 2008 (by Bob Holt's Group)
  - Measured pH, temperature, alkalinity, water level
  - Two sampling methods: bailer and a submersible pump
- Analytes (by Jeff Linder's group)
  - Cations: Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Pb, Se, Zn
  - Anions: $F^-$, $Cl^-$, $SO_4^{2-}$, $Br^-$, $NO_3^-$, $PO_4^{3-}$
  - TOC, TIC
  - pH, Alkalinity
  - VOC
  - $\delta$C13

# Groundwater Type




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

| Metals | Fe (mg/L) | Ba (mg/L) | Pb (ug/L) | Zn (ug/L) | Mn (mg/L) | Cd (ug/L) | Cu (ug/L) |
|---|---|---|---|---|---|---|---|
| Maximum | 11.6 | 0.224 | 65 | 1187 | 0.71 | 3 | 6 |
| Minimum | 0.018 | 0.012 | 6[a] | 4 | 0.002[a] | 2[a] | 2[a] |

- Other metals are non-detectable, such as As

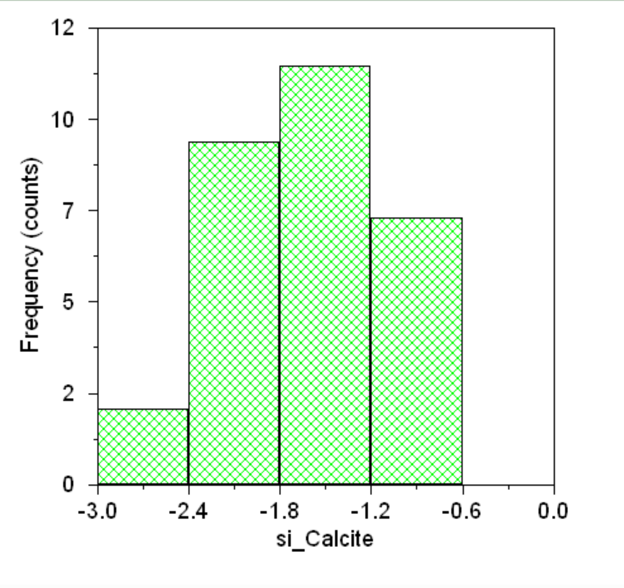
[a] maximum detect limitation

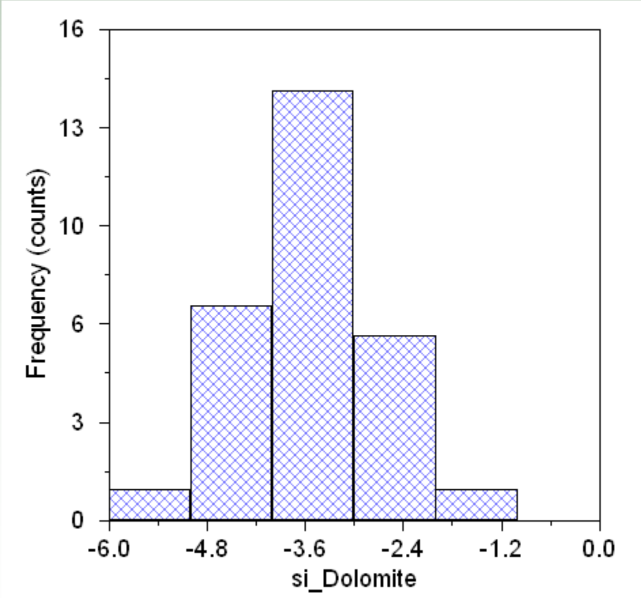
# Carbonate chemistry (1/4)

Mineralogy of the sediments



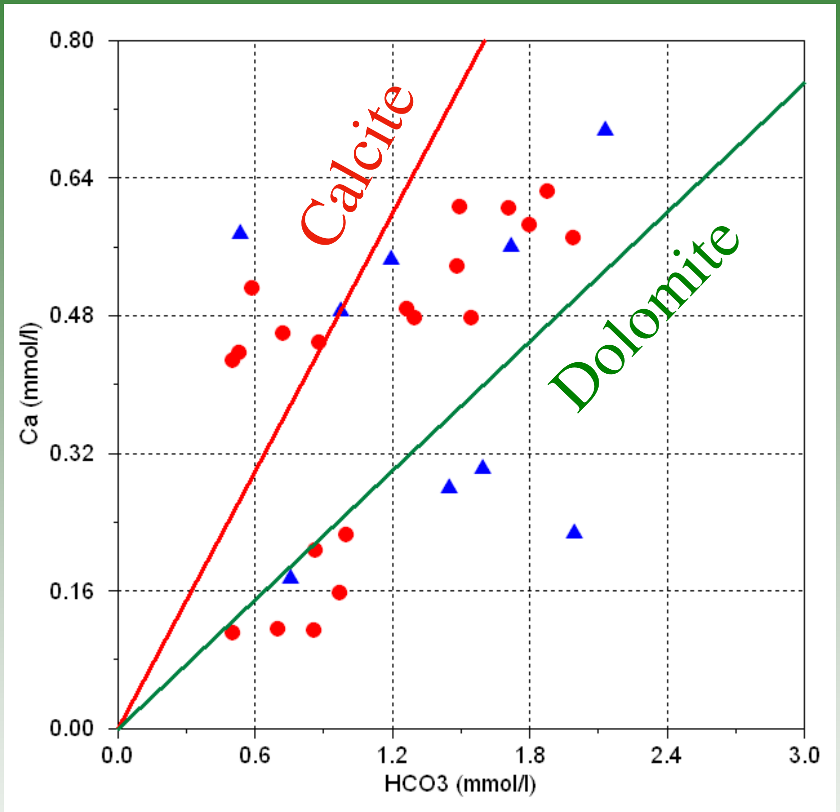
- Preliminary XRD and SEM analyses indicate that the shallow aquifer sediments consist of mainly silicate minerals

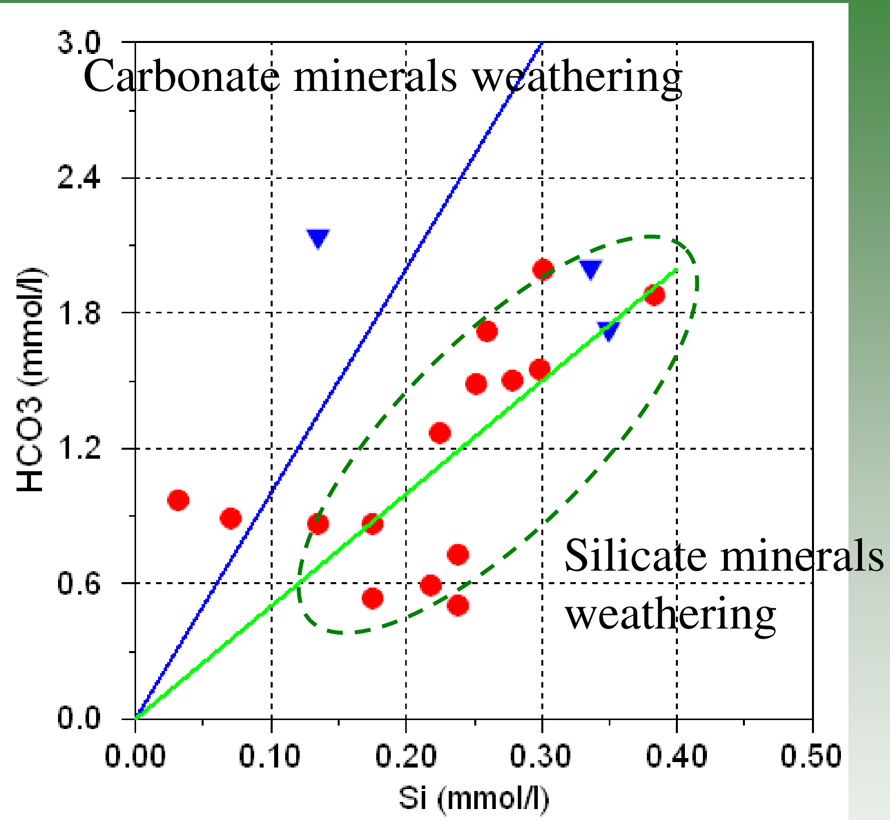



- Carbonate mineral saturation indices show that carbonate minerals (calcite and dolomite) are under saturated with respect to groundwater

# Carbonate chemistry (2/4)



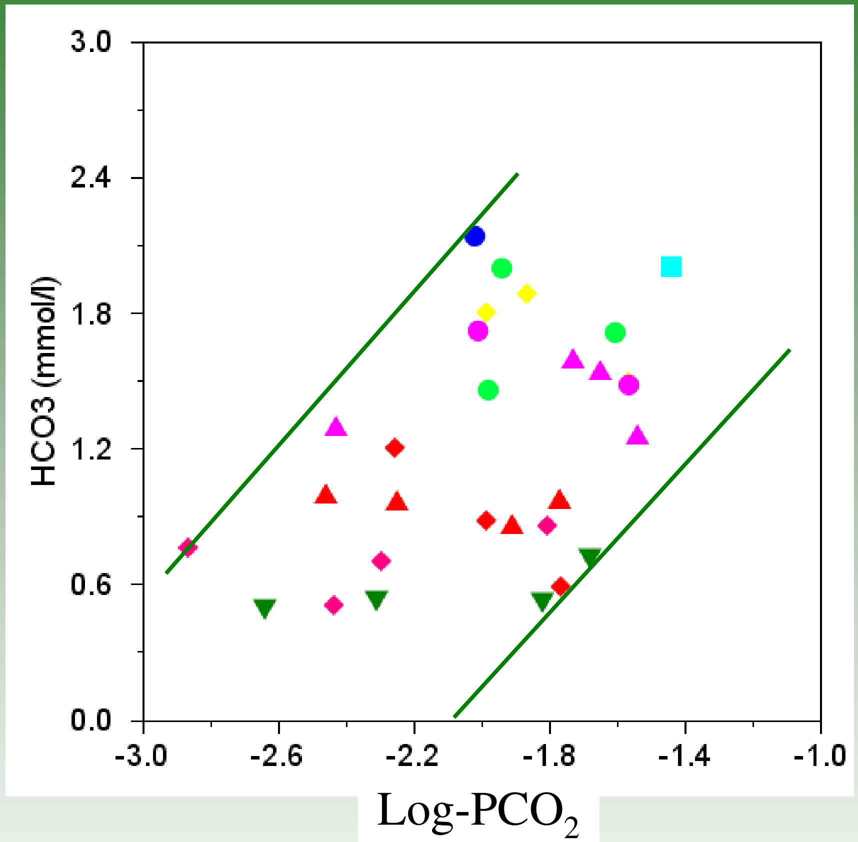



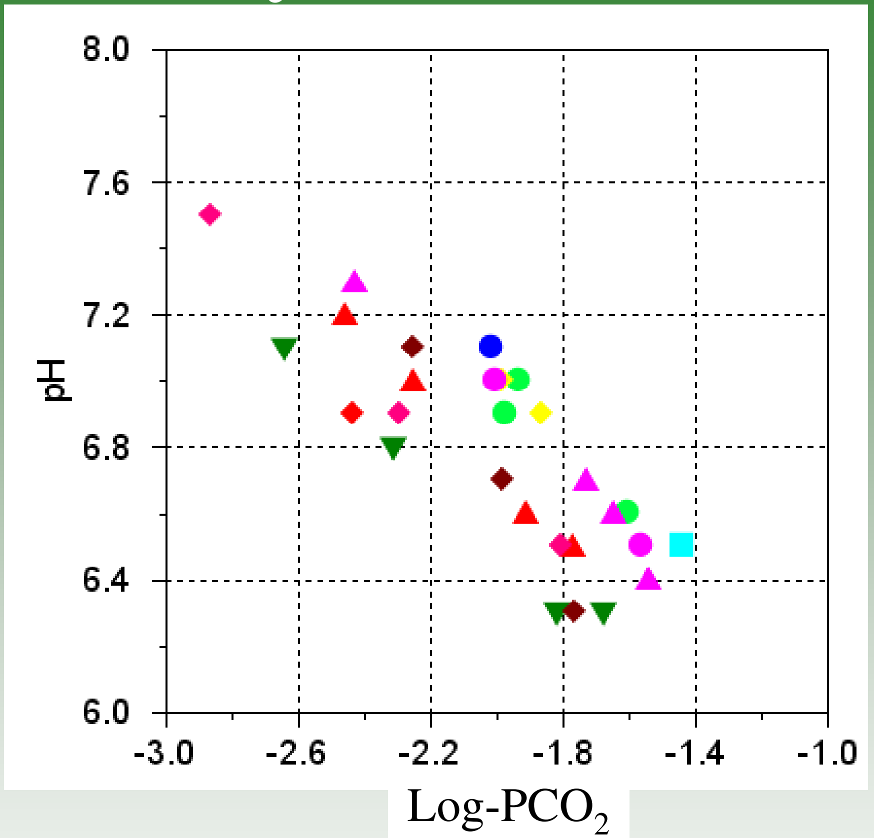

$Dolomite + 2\ CO_2 + 2\ H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$

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

- No obvious correlation between Ca and $HCO_3$; carbonate parameters of groundwater are probably not dominated by carbonate mineral weathering
- $HCO_3$ versus Si indicates groundwater chemistry is dominated by silicate mineral weathering

# Carbonate chemistry (3/4)

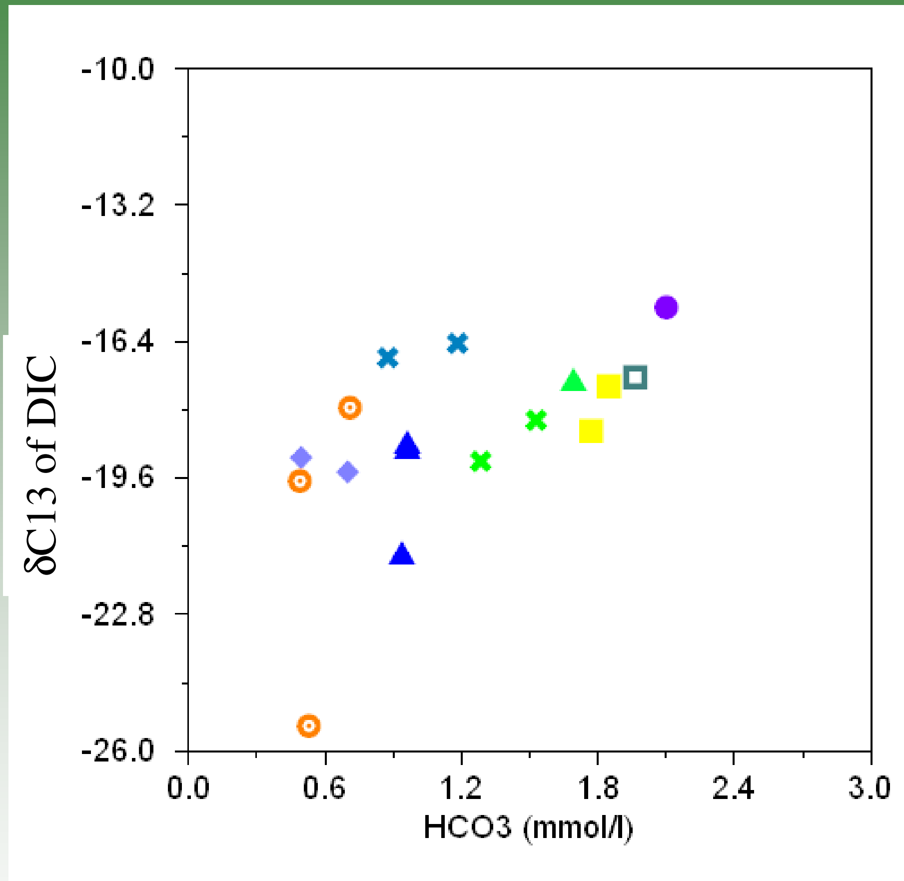


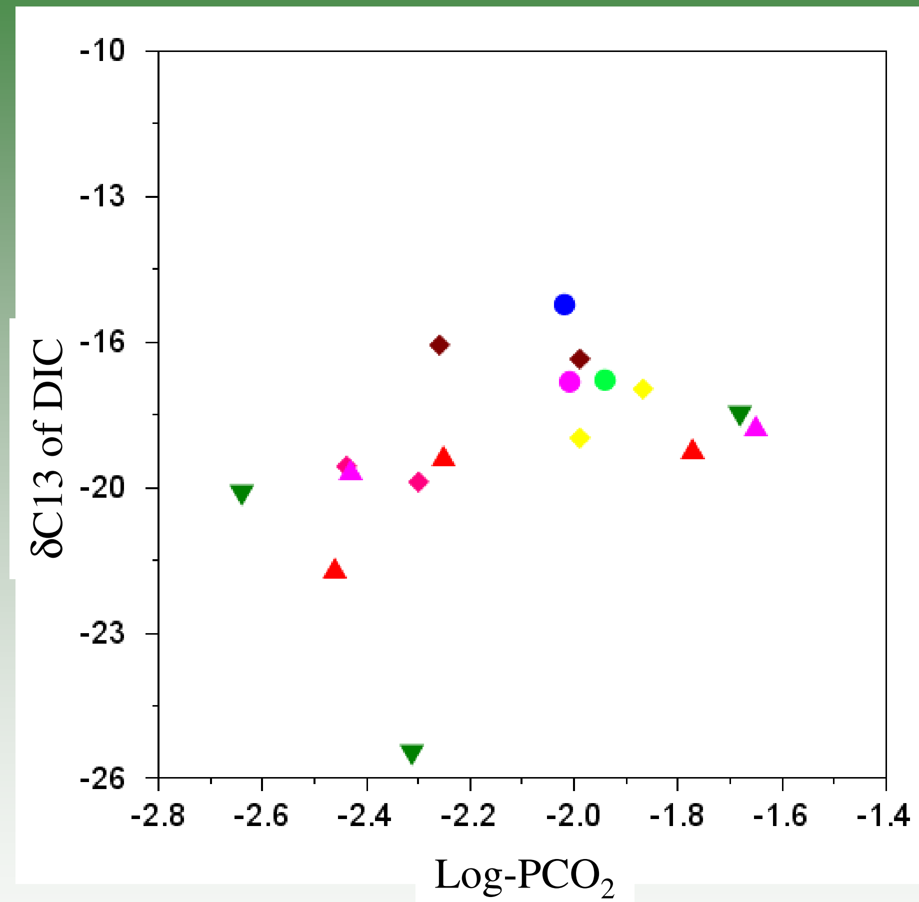




- $HCO_3$ shows an overall increase with log-$PCO_2$ (Log-$CO_2$ pressure)
- pH shows good linear relation with log-$PCO_2$
- This suggests that $CO_2$ may dominate pH and carbonate parameters of groundwater at the cranfield aquifers

# Carbonate chemistry (4/4)

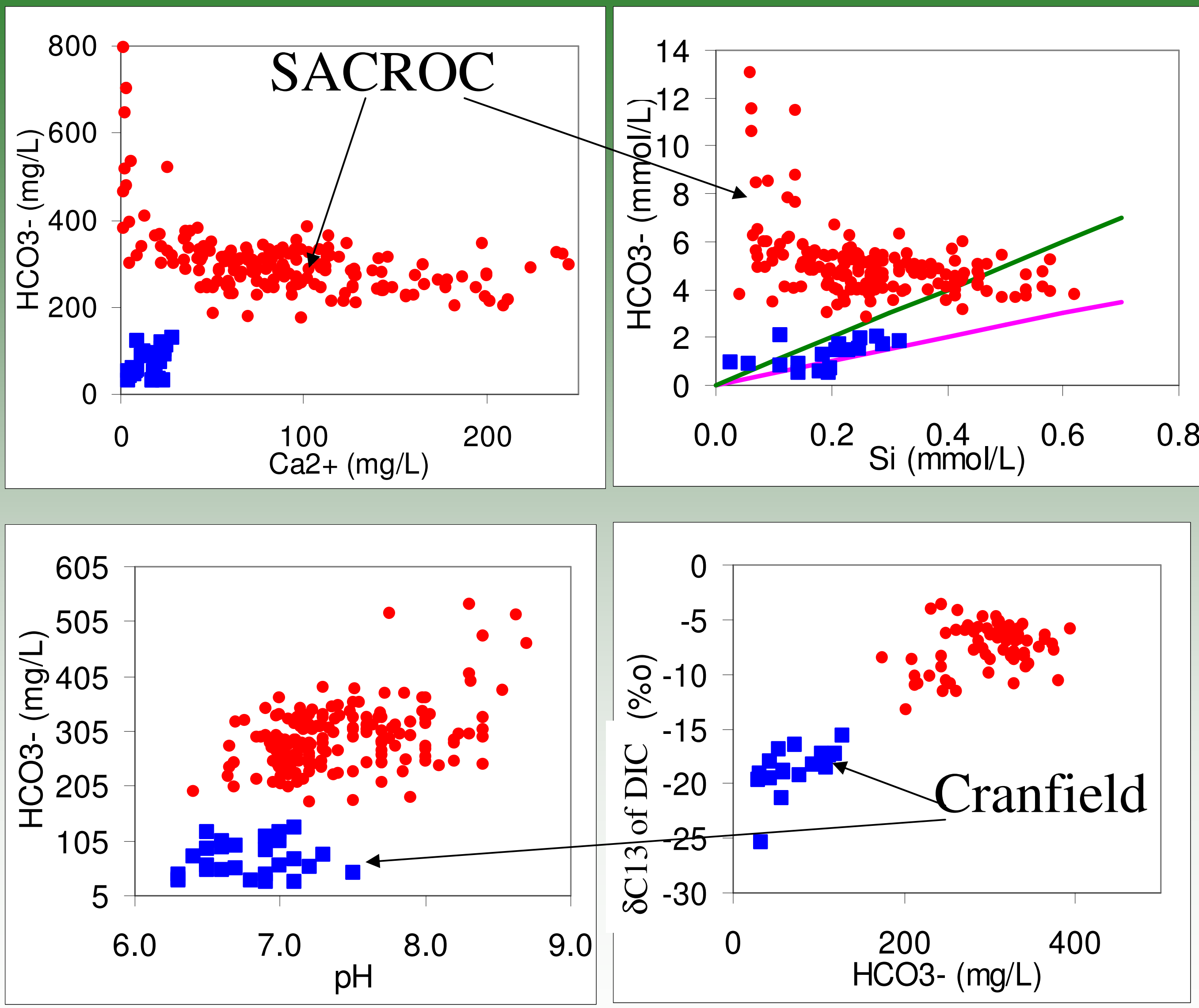
## Stable Carbon Isotope: Ratios (δC13 )




δC13 of dissolved inorganic carbon (DIC) ranges from -14‰ to -26 ‰

# Comparison with SACROC groundwater chemistry




SACROC aquifers (*data from Becky Smyth, SWP project*)

- Sand with carbonate cements
- Carbonate chemistry of groundwater dominated by dedolomitization

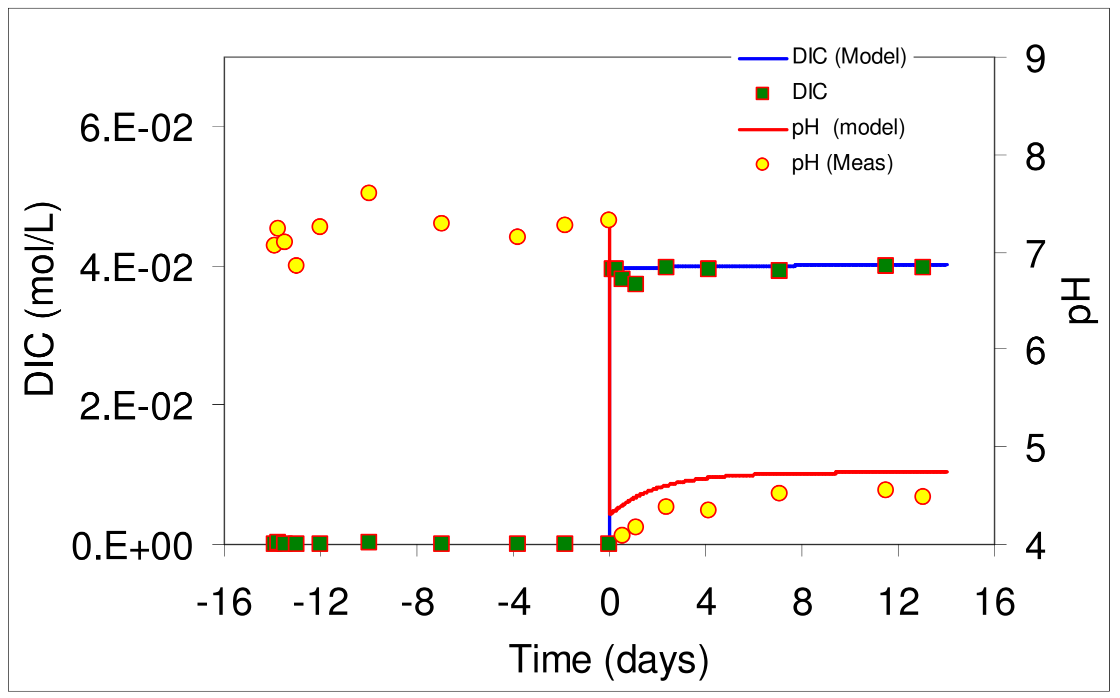
Cranfield aquifers

- Sand with no or little carbonate cements
- Carbonate chemistry of groundwater dominated by $CO_2$ produced from microbial processes

Carbonate parameters show big differences between the two aquifers

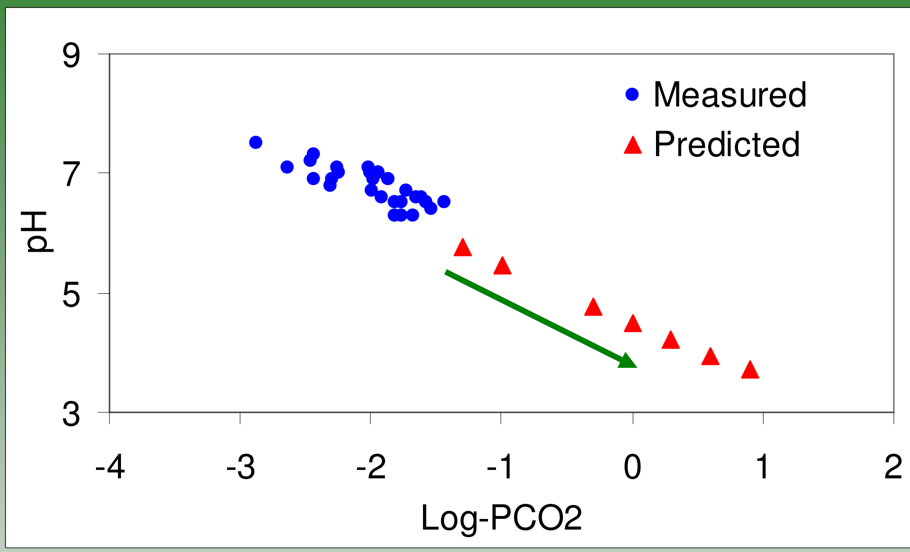
# Batch experiment

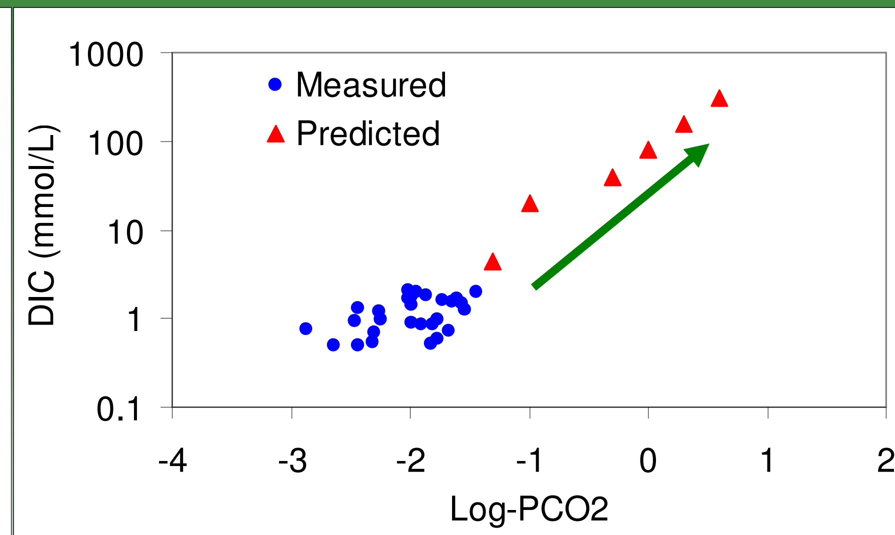
- Rock samples
  - About 95 g
  - Disaggregated, unwashed
- Water
  - 500 mL deionized
  - NaCl added
- First 2 weeks, argon gas was flushed
- Then CO2 gas was bubbled for another 2 weeks, *P*CO2 =1 atm, water was sampled after 1-, 5-, 12-h and 1-, 2-, 4-, 7-, 11-, 13- days

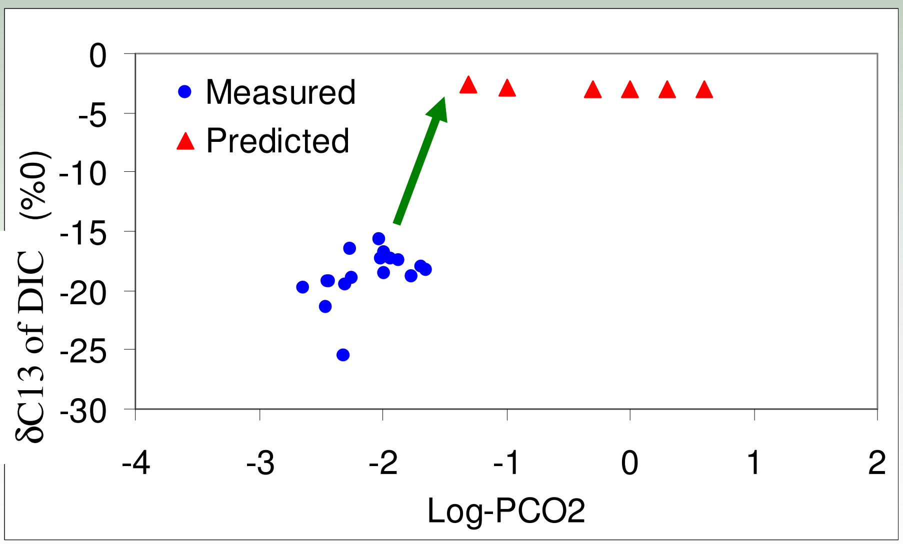



- Laboratory experiments show that in rocks with little or no carbonates, pH decreases sharply when $CO_2$ was introduced into the water-rock system
- Numerical model is used to simulate the batch experiment

# 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

# Summary

- Evidence that the Cranfield aquifers contain little or no carbonate cements
  - SEM and XRD show mainly silicate minerals in the cores
  - Calculated saturation indices of calcite and dolomite show the two minerals are under staturated with respect to groundwater
  - Ratios of HCO3/Si are less than 10
  - Groundwater pH shows good correlation with Log-$PCO_2$
  - δC13 of DIC ranges from -14‰ to -26‰ and may indicate $CO_2$ dissolved in groundwater is from microbial processes

- Groundwater carbonate parameters from Cranfield are compared to those from SACROC, which were dominated by dedolomitization. Significant differences can be seen between the two aquifers in terms of HCO3, HCO3/Si, and δC13 of DIC

# Summary

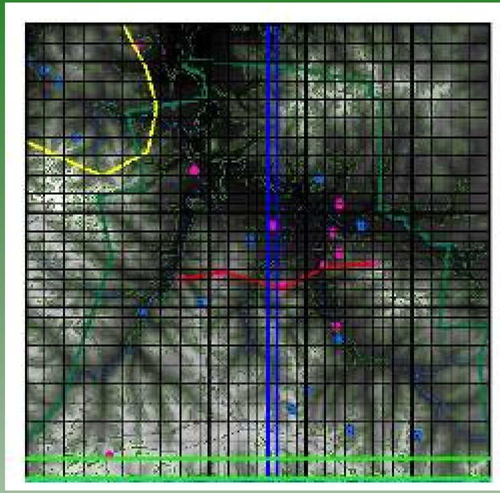
- Laboratory experiments of water-rock-$CO_2$ interactions indicate that pH will decrease sharply once $CO_2$ is introduced into the Cranfield-type aquifers where rocks contain no or little carbonates

- Results of geochemical modeling indicate that carbonate parameters and pH may be used for detecting $CO_2$ leakage at the Cranfield-type aquifers. However, for aquifers containing carbonate minerals, such as SACROC, detecting $CO_2$ leakage using carbonate parameters and pH will be more complicated

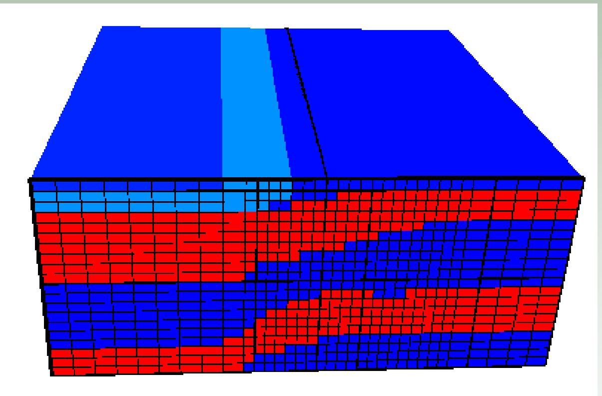
- Using pH and carbonate parameters for detecting $CO_2$ leakage should rely on careful consideration of $CO_2$-water-rocks interactions in the aquifers

# Further work

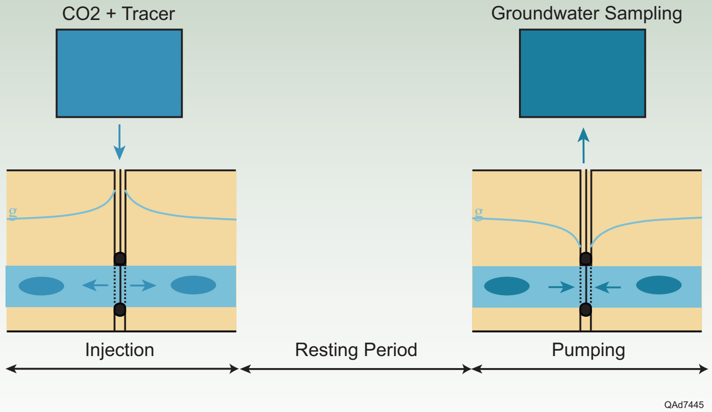
- Groundwater will be sampled from more wells at the Cranfield shallow aquifers;
- 3-Dimensional reactive transport modeling is underway;
- Field push-pull tests for directly injecting $CO_2$ saturated groundwater to shallow aquifers are being prepared



Top view of the model domain



3-D view of the model domain




Schematic showing of push-pull tests at the Cranfield shallow aquifers