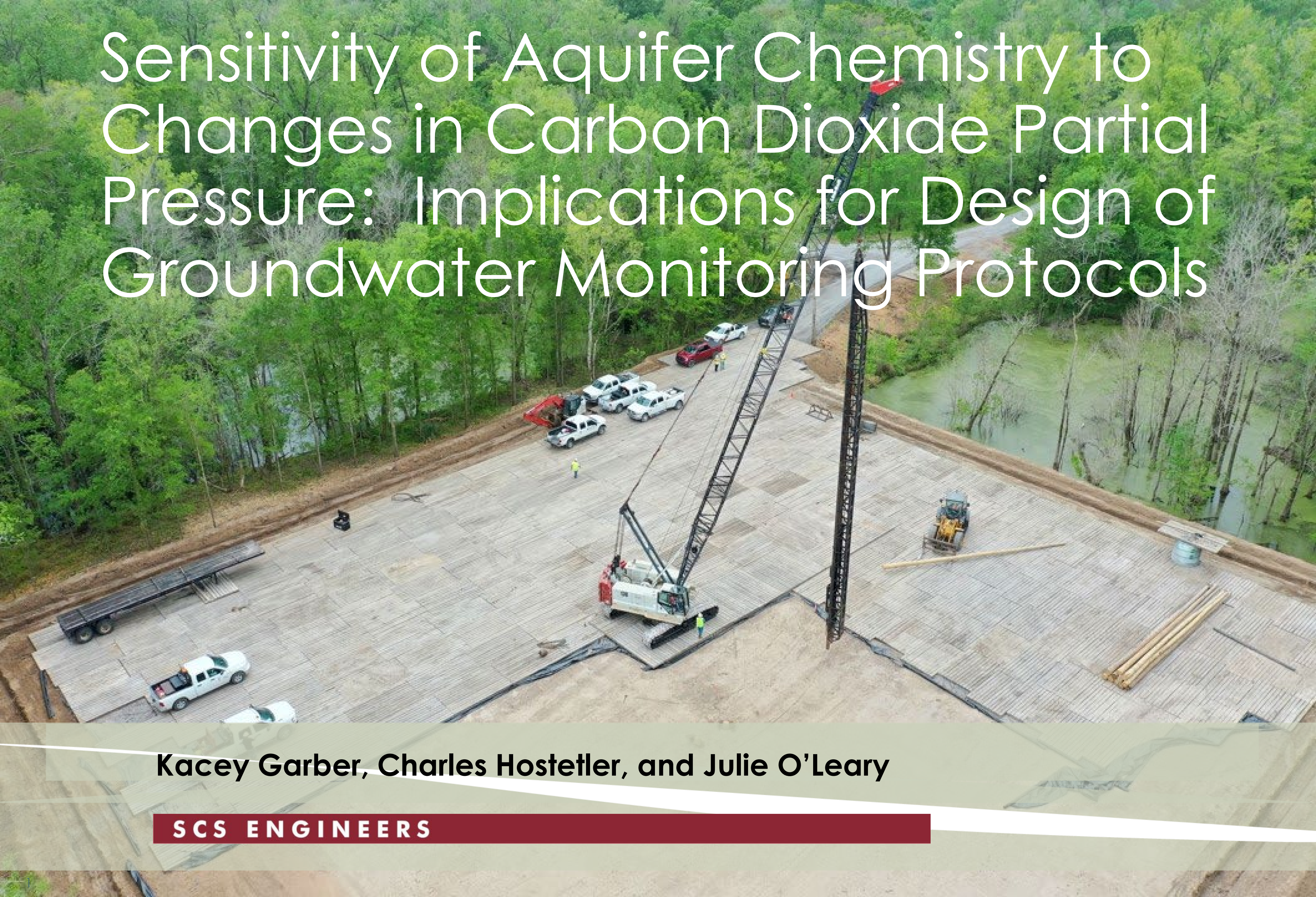
Sensitivity of Aquifer Chemistry to Changes in Carbon Dioxide Partial Pressure: Implications for Design of Groundwater Monitoring Protocols



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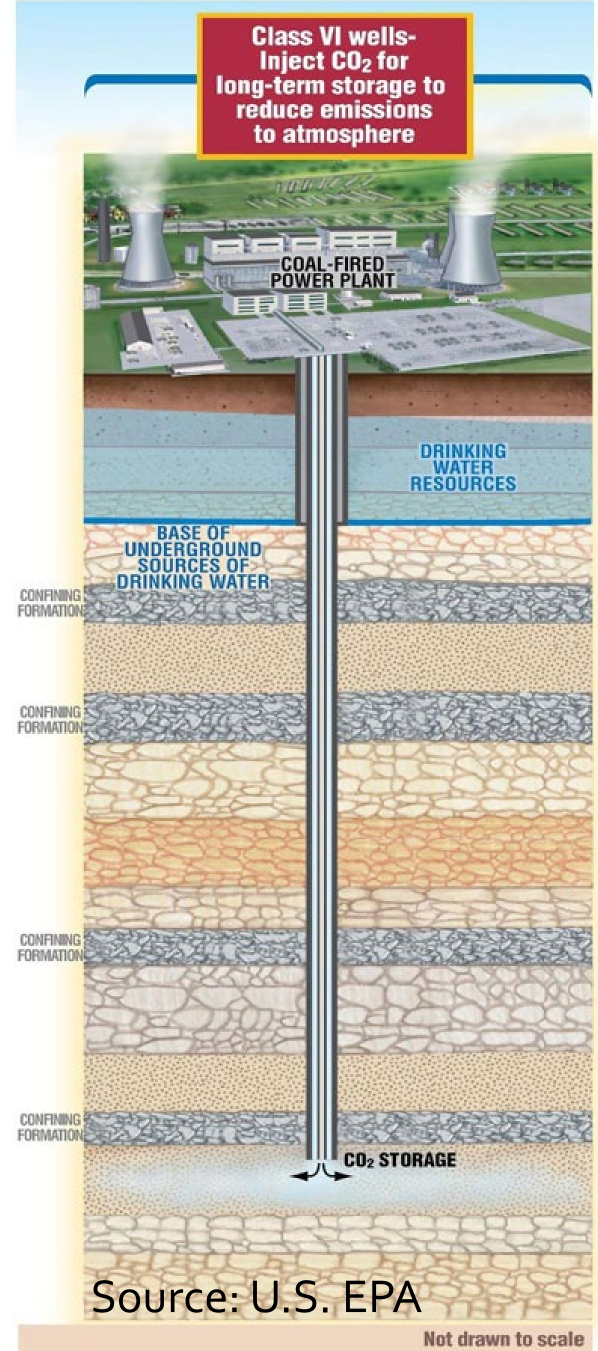
Evolution of Geologic Carbon Sequestration: Opportunity for Process Improvement

- Modern push for geologic sequestration of supercritical CO_2 for countering global warming
- Historical use of CO_2 gas injection for enhanced oil recovery (EOR) since 1972 (U.S. DOE)
- Must submit EPA permit application for injection of CO_2 via Class VI injection well that protects USDWs
- Still optimizing process – only a few issued Class VI injection well permits in the U.S.; many applications in development

Technical Objective

How might we be able to detect CO_2 leakage through testing and monitoring of groundwater?

- Site-specific USDW monitoring programs are required during all project phases.
- Studying and understanding site-specific aquifer geochemistry is important for limiting the cost and complexity of the testing and monitoring program.



Mt. Simon Sandstone: A World Class Carbon Sequestration Target

- Mt. Simon Sandstone (Cambrian) is the target injection zone in Illinois
  - Deep saline aquifer
- Focus of research for Illinois Basin Decatur Project
- First two successful Class VI injection wells
- Mahomet Valley Aquifer System = sole-source aquifer in central and east-central Illinois
  - Overlies the Mt. Simon in some areas and may need monitoring for future targets

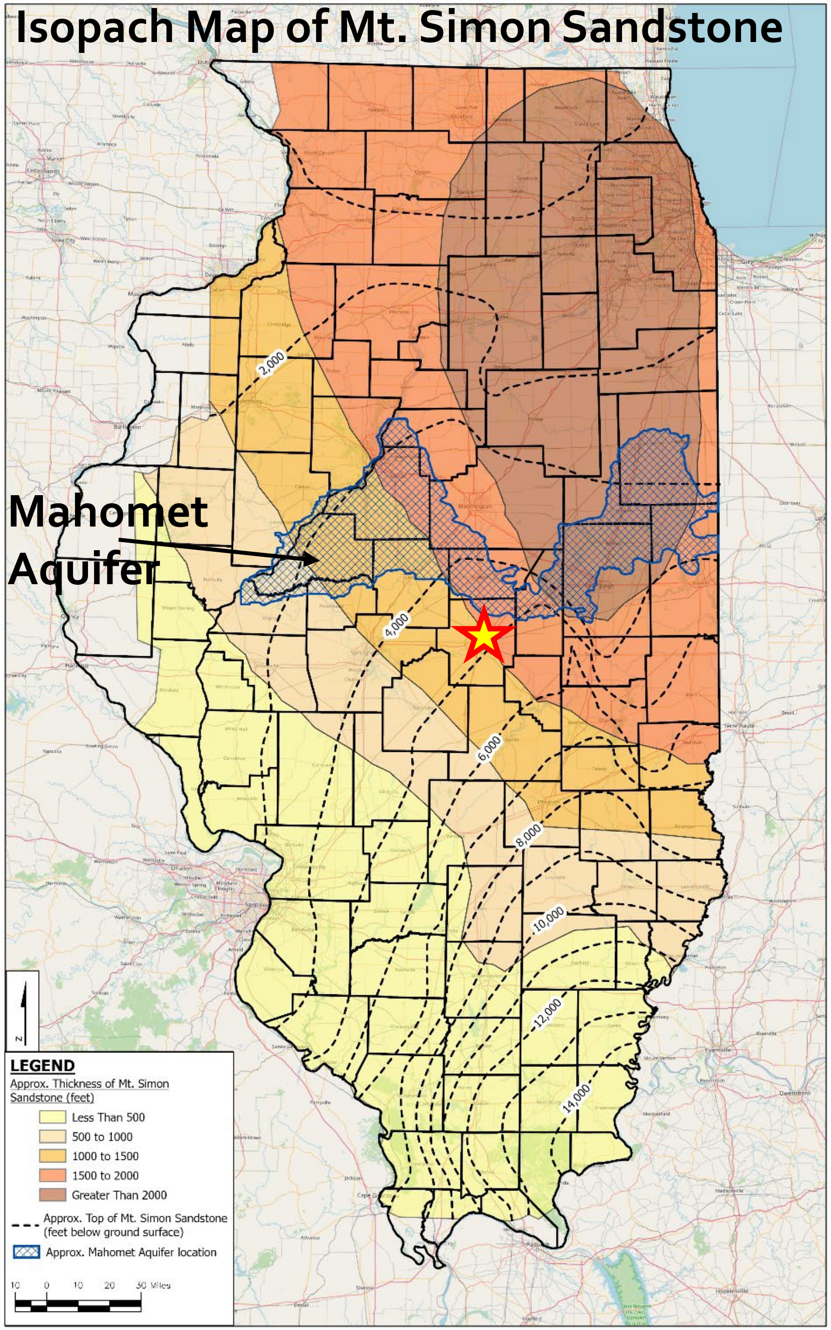
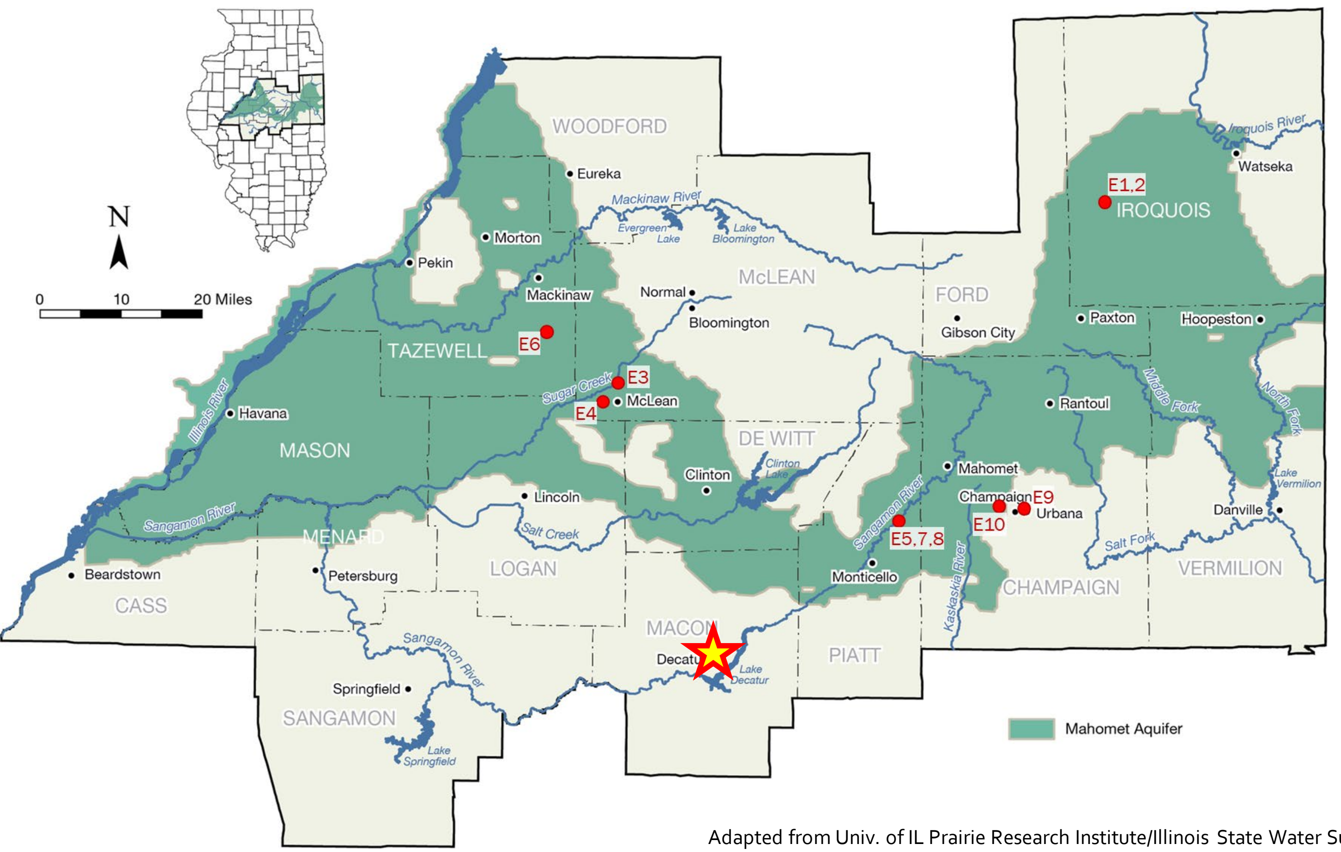


*Figure adapted from the Midwest Geological Sequestration Consortium (2005) and Illinois State Water Survey

Mahomet Valley Aquifer System, IL

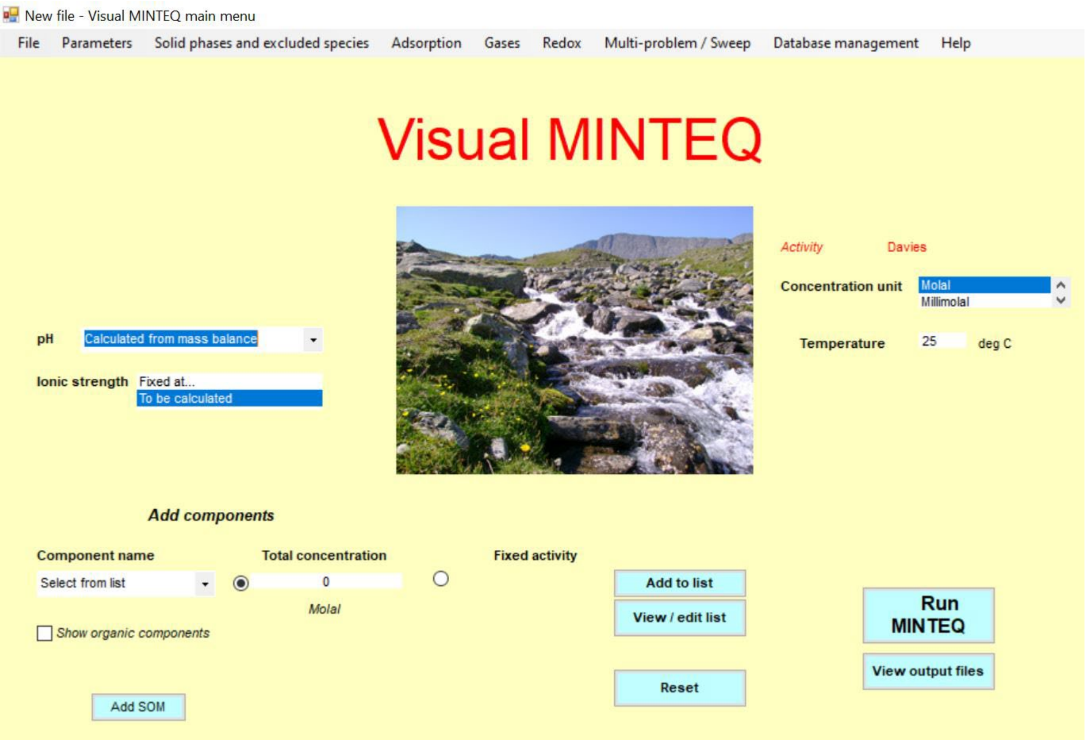


Adapted from Univ. of IL Prairie Research Institute/Illinois State Water Survey

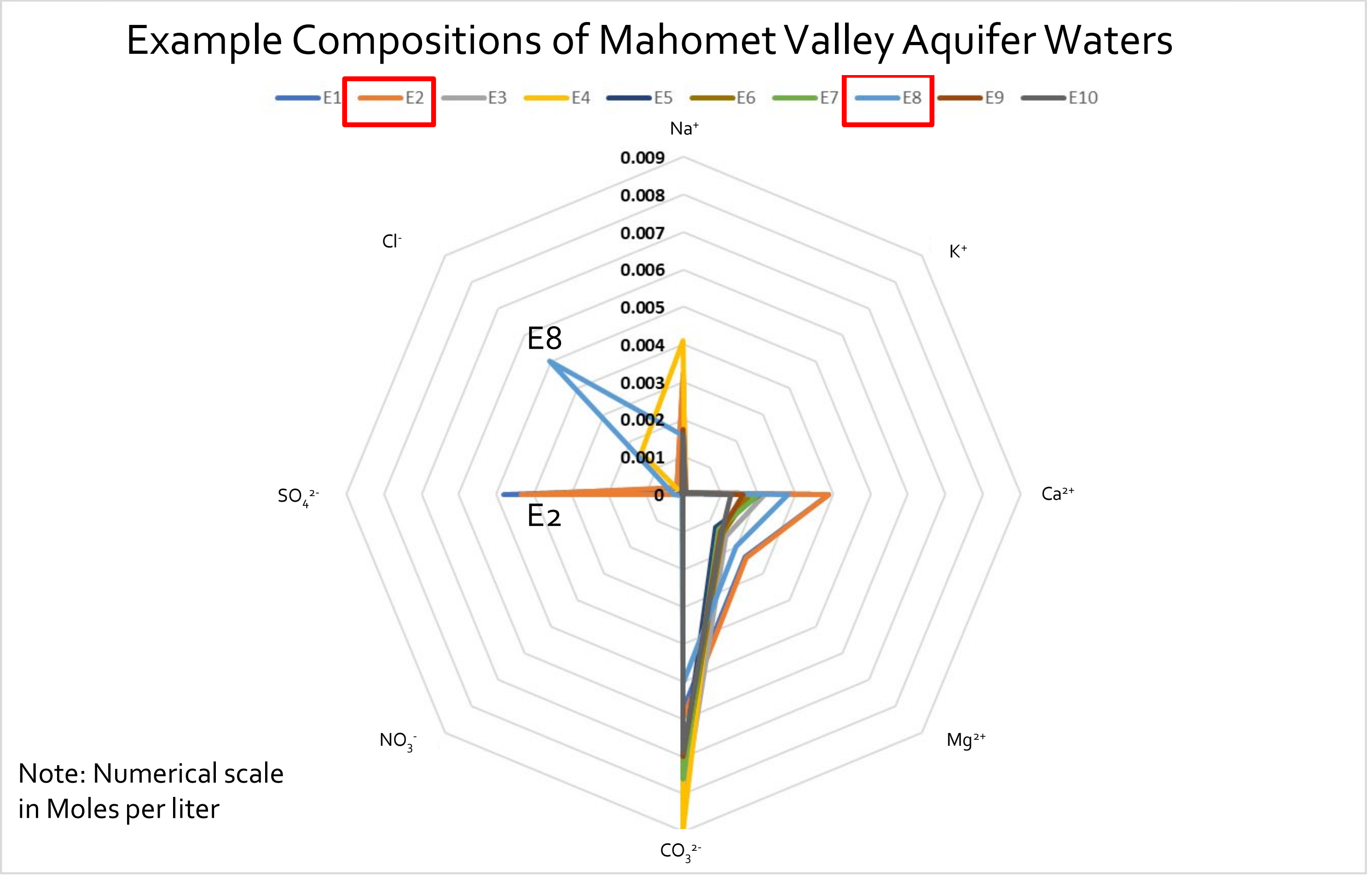
Existing Class VI Wells

- Data source: Panno et al. (1994): Hydrochemistry of the Mahomet Bedrock Valley Aquifer, East-Central Illinois: Indicators of Recharge and Ground-Water Flow
- Ten samples – major and minor cations, anions, trace elements, pH, Eh

Study Design - Use existing data to detect CO_2 leakage through speciation of groundwater:

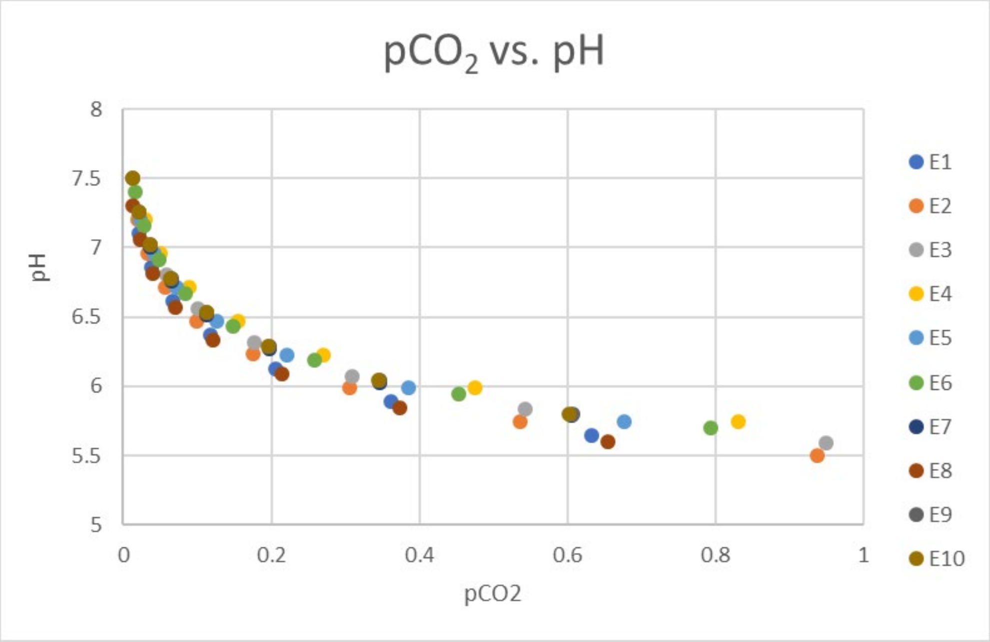


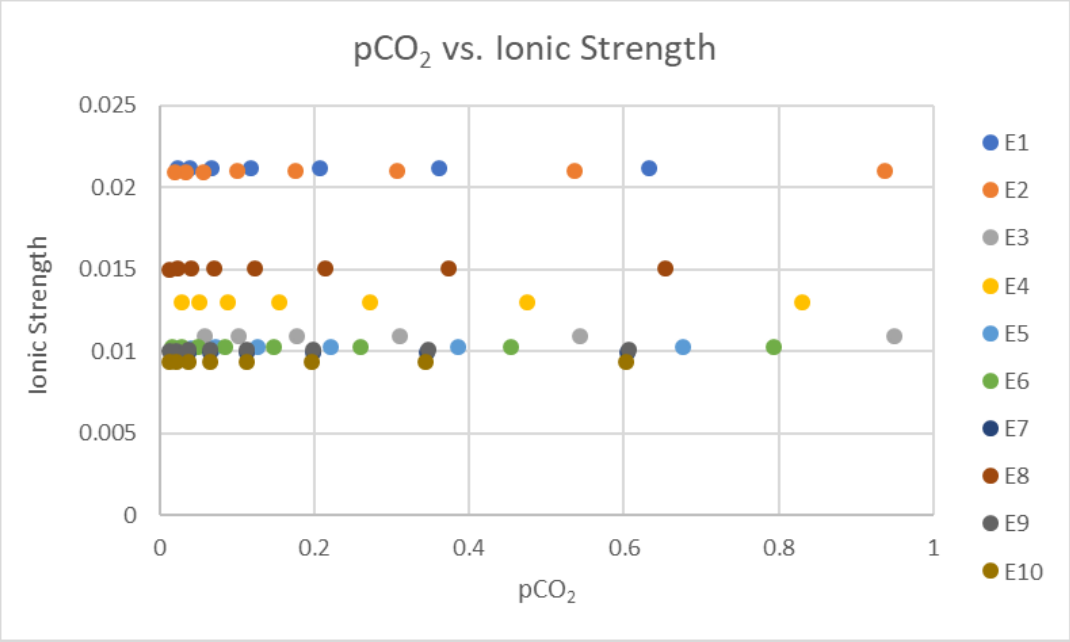
- Thermodynamic modeling using Visual MINTEQ 3.1
- Entered known system variables for the 10 samples from the Mahomet Valley Aquifer System and established a base case pCO_2
- Simulated the effect of increasing the pCO_2 on the geochemical composition of the waters
- Examined species distribution, saturation indices, and equilibrated mass distribution for responses to increasing pCO_2



- Calcium carbonate-dominated waters, with some variation
- Focus here on samples E2 (sulfate-dominant) and E8 (chloride-dominant) to see if different responses occur
- All samples give similar results

System Variables vs. pCO_2



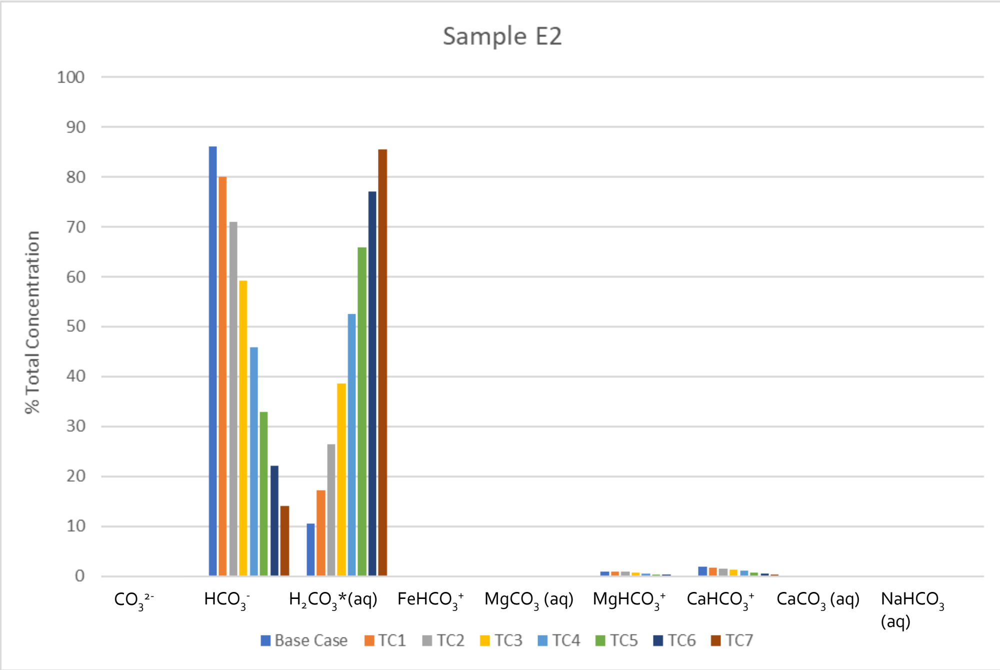


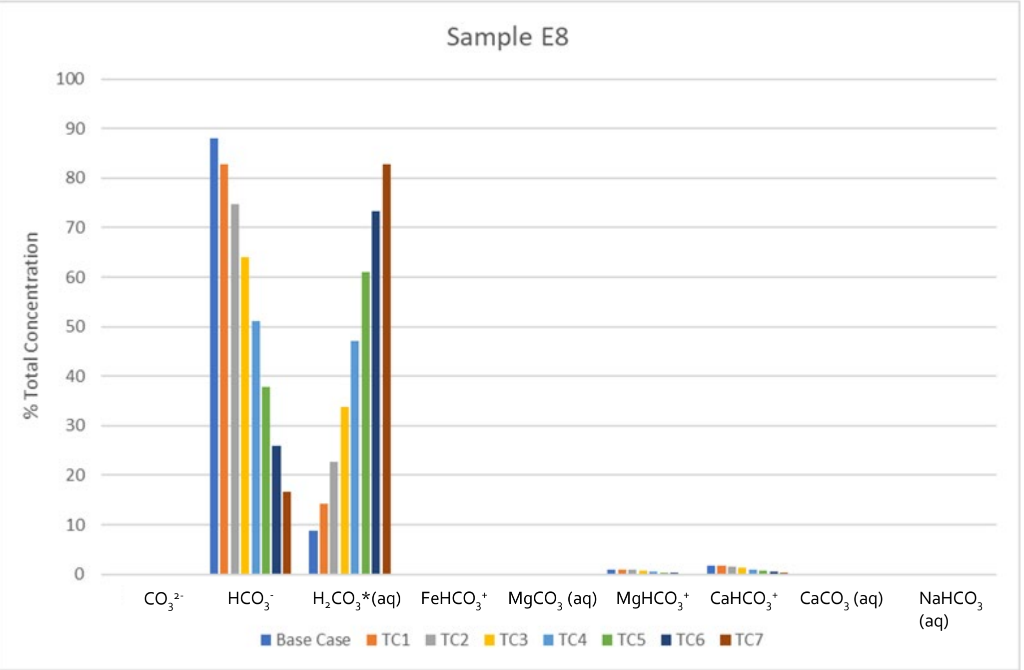
- Sharp initial decrease in pH
- pH decrease levels off as majority of carbonate is converted to carbonic acid

- No change in ionic strength with pCO_2 increase indicates predominance of neutral species

CO_2 (g) + H_2O ⇔ H_2CO_3 (aq)

Species Distribution vs. pCO_2





- Note high initial bicarbonate (HCO_3^-) concentration and progressive decrease in concentration of bicarbonate compounds as pCO_2 increases.
- Progressive increase in carbonic acid (H_2CO_3).
- Shows conversion of carbonate and bicarbonate into carbonic acid.

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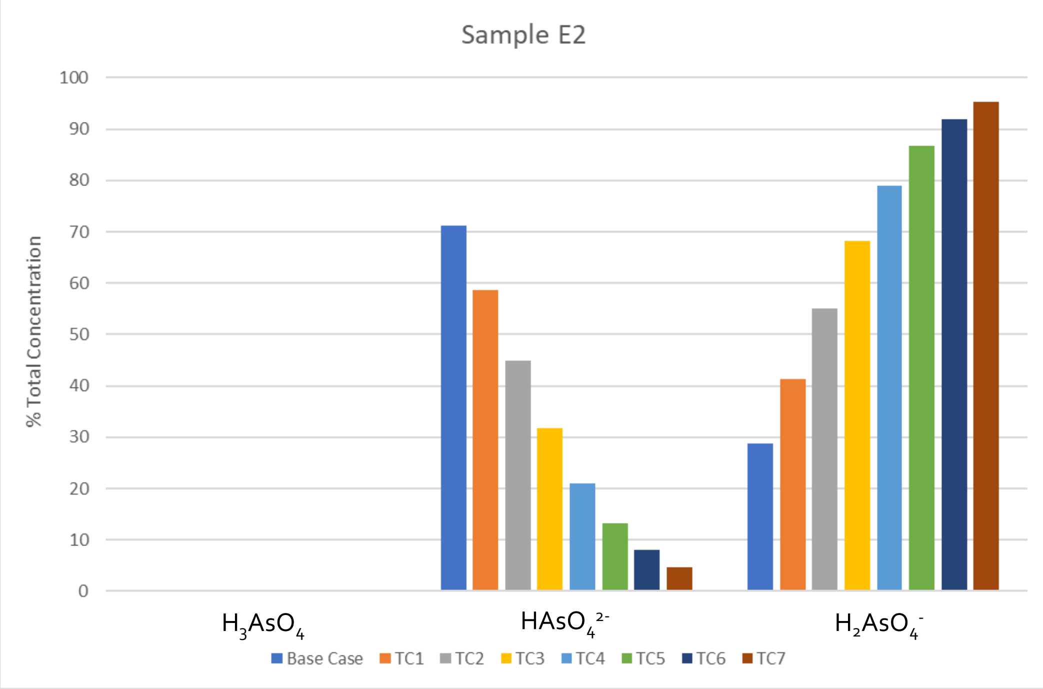
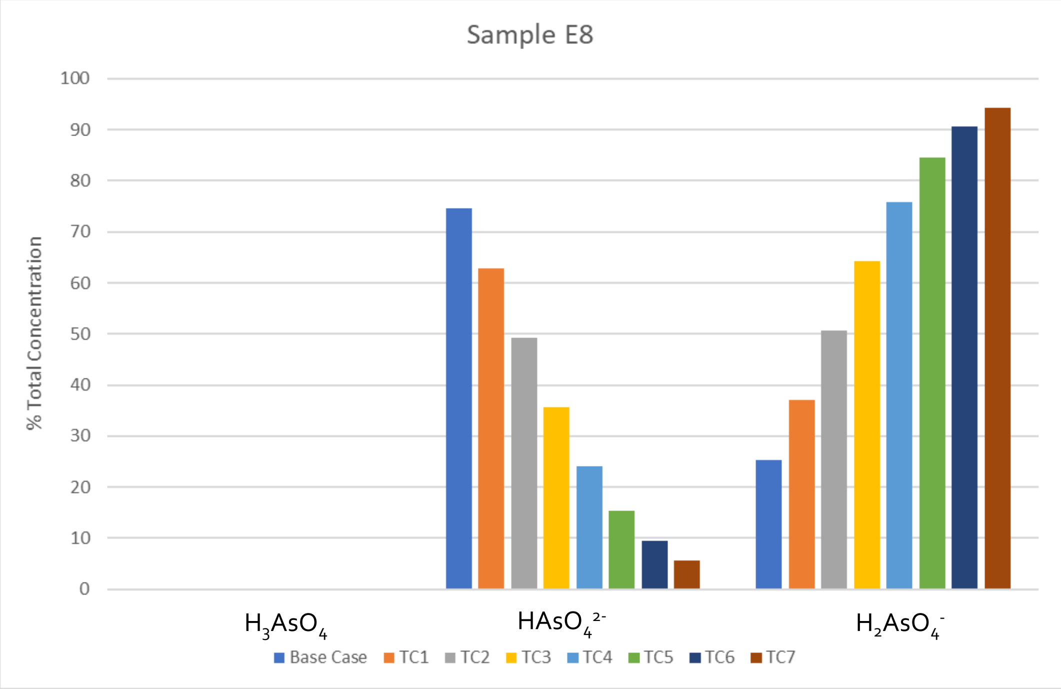
Trace Element Species Distribution vs. pCO_2





- Note high initial hydrogen arsenate ($HAsO_4^{2-}$) concentration and progressive decrease in concentration as pCO_2 increases.
- Progressive increase in dihydrogen arsenate ($H_2AsO_4^-$).
- Shows conversion of hydrogen arsenate into dihydrogen arsenate (and also into arsenic acid in very small concentrations).

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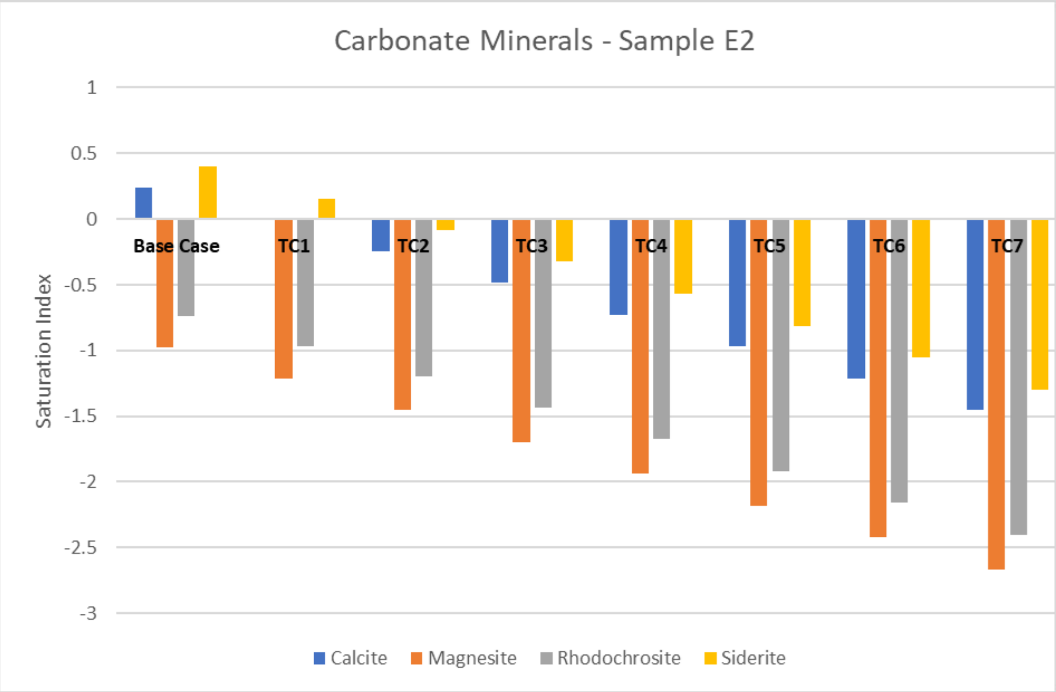
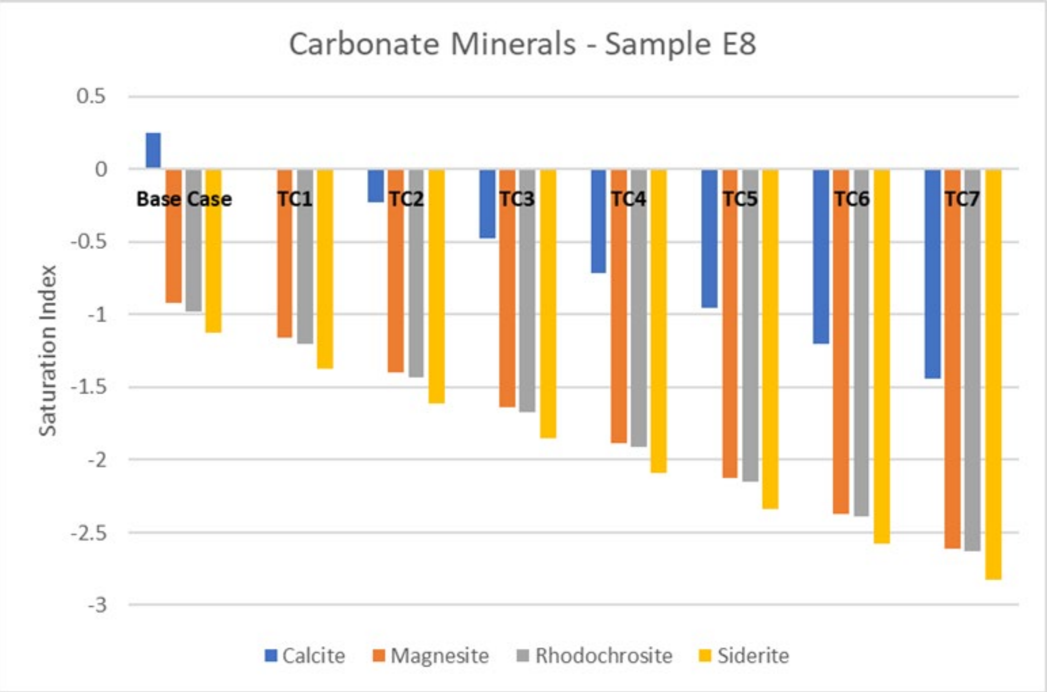
Carbonate Mineral Saturation Indices vs. pCO_2





- Carbonate mineral saturation indices decrease logarithmically with increasing pCO_2.
- Increasing potential to dissolve any carbonate in the aquifer solids and alter the framework of the aquifer pore space.

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Summary of Case Study Results

As pCO_2 increases:

- Groundwater becomes more acidic,
- Carbonate and bicarbonate are converted into carbonic acid,
- Hydrogen arsenate is converted into dihydrogen arsenate, and additionally into arsenic acid, and
- Silicate and sulfate SI's are unaffected, while carbonate SI's strongly decrease.

Recommendations for Monitoring Programs

1. Monitoring program should be constructed based on the outcome of site-specific geochemical and flow and transport modeling.
2. As more site-specific data are obtained during the operational phase, the models should be updated and their predictions re-examined.
3. Alternative methods (e.g., isotopic and dissolved trace gases) exist and should be considered when the monitored unit has low total dissolved solids.

Recommendations for Monitoring Programs

4. For relatively dilute waters (i.e., Mahomet Aquifer System), changes in pH, total dissolved carbonate, and strong-complexing anions will be the strongest geochemical indicators of initial CO_2 leakage
   - For these dilute aquifers, even small variations in composition can lead to false positives in the monitoring network.
   - **Establishing representative baseline** is key to a cost-effective and robust testing and monitoring program.
   - Optimizing the monitoring parameter list to **maximize statistical power** in the monitoring network is also key.