

Assessing Potential Impacts of CO₂ Leakage on Shallow Groundwater Quality at the SECARB Phase III Early Test site Using Single-well Push-Pull Tests

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A single-well push-pull test was conducted at the Cranfield shallow aquifer, the SECARB Phase III early test site for assessing potential impacts of CO₂ leakage on groundwater quality. Total 3800 liter of groundwater equilibrated with CO₂ gas at a partial pressure of 1.10^5 Pa was injected in a confined sand interval at approximately 70 m depth. NaBr solution was added to the injected solution as tracer. The injected groundwater incubated within the interval for roughly 2 days. Chemical parameters (pH, temperature, alkalinity, and electric conductivity) were measured on-site and water samples were collected for chemical (major ions, trace elements, and dissolved inorganic carbon, DIC) as well as for stable carbon isotopic analyses. Mineralogy analysis using XR-D and SEM techniques indicates silicates are dominant in aquifer sediments.

Concentrations of tracer, Br⁻ of the recovered samples display mixing background water and the injected solution. Major ions, especially, Ca, Mg, K and Si show obvious enrichment, indicating mobilization of these ions occurred from aquifer sediments to groundwater and may be dominated by dissolution of silicates and possible carbonate minerals. $d^{13}C$ of DIC of the recovered samples may also suggest potential dissolution of carbonates. Concentrations of trace elements show mobilization after the groundwater with CO₂ was injected. Mobilization of trace elements could be due to co-dissolution of silicates and carbonates and desorption from surface of aquifer sediments. However, mass balance calculation suggests that ion mobilization is mild and therefore, potential risks of CO₂ are low, especially for arsenic and lead which concentrations of the recovered samples are ~30 times smaller than the EPA maximum contamination level.

Results of the single-well push-pull test were also compared to a laboratory batch experiment of water-rock-CO₂ interactions. Overall reaction rates of most ions estimated are higher in the batch experiments than in the push-pull test. Such differences could be due to larger reactive surface area in that batch experiment. Our study shows single-well push-pull test appears to be a convenient approach for assessing potential impacts of CO₂ leakage on drinking water resources at geological CO₂ sequestration sites.

Low temperature-pressure batch experiments and field push-pull tests: Assessing potential effects of an unintended CO₂ release from CCUS projects on groundwater chemistry.

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Carbon Capture Utilization and Storage projects (CCUS), where CO₂ is captured at point sources such as power stations and compressed into a supercritical liquid for underground storage, has been proposed to reduce atmospheric CO₂ and mitigate global climate change. Problems may arise from CO₂ releases along discreet pathways such as abandoned wells and faults, upwards and into near surface groundwater. Migrating CO₂ may inversely impact fresh water resources by increasing mineral solubility and dissolution rates and mobilizing harmful trace elements including As and Pb. This study addresses the impacts on fresh water resources through a combination of laboratory batch experiments, where aquifer sediment are reacted in their corresponding groundwater in 100% CO₂ environments, and field push-pull tests where groundwater is equilibrated with 100% CO₂, reacted in-situ in the groundwater system, and pulled out for analyses. Batch experiments were performed on aquifer material from carbonate dominated, mixed carbonate/siliclastic, and siliclastic dominated systems. A mixed siliclastic/carbonate system was chosen for the field based push-pull test.

Batch experiment results suggest carbonate dissolution increased the concentration of Ca, Mg, Sr, Ba, Mn, U and HCO₃⁻ in groundwater. In systems with significant carbonate content, dissolution continued until carbonate saturation was achieved at approximately 1000 hr. Silicate dissolution increased the conc. of Si, K Ni and Co, but at much lower rates than carbonate dissolution. The elements As, Mo, V, Zn, Se and Cd generally show similar behavior where concentrations initially increase but soon drop to levels at or below the background concentrations (~48 hours). A Push-Pull test on one aquifer system produced similar geochemical behavior but observed reaction rates are higher in batch experiments relative to push-pull tests.

Release of CO₂ from CCUS sites into overlying aquifer systems may adversely impact groundwater quality primarily through carbonate dissolution which releases Ca and elements that substitute for Ca in crystal lattices. Silicate weathering releases primarily Si and K at lower rates. Chemical changes with the addition of CO₂ may initially mobilize As, Mo, V, Zn, Se and Cd but these elements become immobile in the lowered pH water and sorb onto aquifer minerals. A combined laboratory batch experiment and field push-pull test in fresh water aquifers overlying CCUS projects will best characterize the response of the aquifer to increased pCO₂. The long experimental duration of the batch experiments may allow reactions to reach equilibrium however; reaction rates may be artificially high due to increased mineral surface areas. Field based push-pull tests offer a more realistic water rock ratio and test a much larger volume of aquifer material but the test must be shorter in duration because the high pCO₂ water is subject to mixing with low pCO₂ background water and migration away from the test well with groundwater flow. A comparison of the two methods best characterizes the potential effects on groundwater chemistry

Detecting potential impacts of deep subsurface CO₂ injection on shallow drinking water

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Presented here are results from one aspect of collective research conducted at Gulf Coast Carbon Center, BEG, Jackson School at UT Austin. The biggest hurdle to public acceptance of CCS is to show that drinking water resources will not be impacted. Since late 1990s our group has been supported by US DOE NETL and private industry to research how best to detect potential impacts to shallow (0 to ~0.25 km) subsurface drinking water from deep (~1 to 3.5 km) injection of CO₂. Work has and continues to include (1) field sampling and testing, (2) laboratory batch experiments, (3) geochemical modeling. The objective has been to identify the most sensitive geochemical indicators using data from research-level investigations, which can be economically applied on an industrial-scale. The worst-case scenario would be introduction of CO₂ directly into drinking water from a leaking wellbore at a brownfield site. This is unlikely for a properly screened and/or maintained site, but needs to be considered. Our results show aquifer matrix (carbonate vs. clastic) to be critical to interpretation of pH and carbonate (DIC, Alkalinity, and $\delta^{13}\text{C}$ of DIC) parameters because of the influence of water-rock reaction (buffering vs. non-buffering) on aqueous geochemistry.

Field groundwater sampling sites to date are Cranfield, MS and SACROC, TX CO₂-EOR oilfields. Two major aquifer types are represented, one dominated by silicate (Cranfield) and the other by carbonate (SACROC) water-rock reactions. We tested sensitivity of geochemical indicators (pH, DIC, Alkalinity, and $\delta^{13}\text{C}$ of DIC) by modeling the effects of increasing pCO₂ on aqueous geochemistry, and laboratory batch experiments, both with partial pressure of CO₂ gas (pCO₂) at 1×10^5 Pa (1 atm). Aquifer matrix and groundwater data provided constraints for the geochemical models. We used results from modeling and batch experiments to rank geochemical parameter sensitivity to increased pCO₂ into weakly, mildly and

strongly sensitive categories for both aquifer systems. DIC concentration is strongly sensitive to increased $p\text{CO}_2$ for both aquifers; however, CO_2 outgassing during sampling complicates direct field measurement of DIC.

Interpretation of data from in-situ push-pull aquifer tests is ongoing and will be used to augment results summarized here. We are currently designing groundwater monitoring plans for two additional industrial-scale sites where we will further test the sensitivity and utility of our sampling approach.