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Assessing risk to fresh water resources from long term CO₂ injection – laboratory and field studies

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Abstract

In developing a site for geologic sequestration, one must assess potential consequences of failure to adequately contain injected carbon dioxide (CO₂). Upward migration of CO₂ or displacement of saline water because of increased pressure might impact protected water resources 100s to 1000s of meters above a sequestration interval. Questions posed are: (1) Can changes in chemistry of fresh water aquifers provide evidence of CO₂ leakage from deep injection/sequestration reservoirs containing brine and or hydrocarbons? (2) What parameters can we use to assess potential impacts to water quality? (3) If CO₂ leakage to freshwater aquifers occurs, will groundwater quality be degraded and if so, over what time period?

Modeling and reaction experiments plus known occurrences of naturally CO₂-charged potable water show that the common chemical reaction products from dissolution of CO₂ into freshwater include rapid buffering of acidity by dissolution of calcite and slower equilibrium by reaction with clays and feldspars. Results from a series of laboratory batch reactions of CO₂ with diverse aquifer rocks show geochemical response within hours to days after introduction of CO₂. Results included decreased pH and increased concentrations of cations in CO₂ experimental runs relative to control runs using argon (Ar). Some cation (Ba, Ca, Fe, Mg, Mn, and Sr) concentrations increased over and an order of magnitude during CO₂ runs. Results are aquifer dependant in that experimental vessels containing different aquifer rocks showed different magnitudes of increase in cation concentrations.

Field studies designed to improve understanding of risk to fresh water are underway in the vicinity of (1) SACROC oilfield in Scurry County, Texas, USA where CO₂ has been injected for enhanced oil recovery (EOR) since 1972 and (2) the Cranfield unit in Adams County, Mississippi, USA where CO₂ EOR is currently underway. Both field studies are funded by the U.S. Department of Energy (DOE) regional carbon sequestration partnership programs and industrial sponsors. Preliminary results of groundwater monitoring are currently available for the SACROC field study where researchers investigated 68 water wells and one spring during five field excursions between June 2006 and July 2008. Results to date show no trend of preferential degradation below drinking water standards in areas of CO₂ injection (inside SACROC) as compared to areas outside of the SACROC oil field.

Keywords: geologic sequestration; water resources; laboratory experiments; increased pH; cations; groundwater sampling.

1. Introduction

Site selection for geologic sequestration (GS) is the key element in assuring that carbon dioxide (CO₂) will be retained in an appropriate receiving formation for geologically significant periods of time. Restriction of fluid injection permits to properly selected sites is mandated by the Safe Drinking Water Act of 1974 (U.S. House of Representatives, 1974), and managed by the United States Environmental Protection Agency (USEPA) Underground Injection Control (UIC) Program. In a correctly selected GS site there should be negligible transport of CO₂ out of the injection formation, and migration would be limited to diffusion into confining zones. Underground sources of drinking water (USDWs) near a correctly selected site would not be impacted by CO₂ injection, thereby meeting USEPA requirements to protect human drinking water supplies. However, it is prudent to assess potential impacts of (1) failure to contain injected CO₂ in the receiving formation, and (2) displacement of high-salinity fluid (brine) into USDWs. Potential errors in site selection considered here are presence of moderate to high permeability flow paths such as a vertically transmissive fault or improperly plugged well, along which CO₂ and/or brine could migrate. The possibility of impacts to USDWs is the focus of this brief paper. A USDW is defined in the USEPA Proposed Rule for Permitting Full-Scale Geologic Sequestration Projects (July 2008) as: *An aquifer or portion of an aquifer that supplies any public water system or that contains a sufficient quantity of groundwater to supply a public water system, and currently supplies drinking water for human consumption, or that contains fewer than 10,000 mg/l total dissolved solids and is not an exempted aquifer*. By regulation CO₂ would be injected below the deepest USDW and separated from it by a confining zone (i.e. low permeability seal).

In the following sections we present results from laboratory experiments conducted to assess chemical by-products of reactions between injected CO₂, aquifer host rocks, and fresh groundwater. We then present results from a field-based study of groundwater quality overlying the Scurry Area Canyon Reef Operators Committee (SACROC) oilfield in Scurry County, Texas, U.S.A. CO₂ has been injected at SACROC for enhanced oil recovery (EOR) since 1972 making this an ideal natural laboratory in which to observe potential impacts of CO₂ to groundwater. This work has been funded by (1) the Gulf Coast Carbon Center (GCCC) industrial sponsor program at the Bureau of Economic Geology (BEG) at The University of Texas at Austin, (2) the Department of Energy National Energy Technology Laboratory (DOE/NETL) through the Southwest Regional Partnership for Carbon Sequestration (SWP) administered by New Mexico Tech, and (3) Kinder Morgan CO₂ pipeline and production companies.

2. CO₂-rock reaction fundamentals

Most studies of how CO₂ dissolves in water and reacts with the host rock have considered injection zones at greater than 1 km depth and focused on the trapping of CO₂ in mineral phases (Rochelle et al, 2004, Gunter et al., 2004, Worden and Smith, 2004). CO₂-solubility dependence on pressure, temperature, and salinity is well known. Field observations at the Frio (e.g. Karaka et al., 2006 and Hovorka et al., 2006) and Weyburn (IEA, 2005) test sites, and simulations based on observations at the sites, have documented rock-brine-CO₂ reactions at 1,500 m depths in 100,000 mg/L basinal brines. Under these conditions, fluids are strongly reducing (methane saturated) and CO₂ is supercritical (Knauss et al., 2005). Under most circumstances CO₂ will dissolve in water and lower pH. In a system containing reactive mineral phases, the decrease in pH is buffered by dissolution of Ca/Mg/Fe-bearing silicate minerals (Gunter et al., 1993). High CO₂ content causes continued dissolution of silicates, and precipitation of clay minerals, carbonates, and quartz when the acidity has been reduced by silicate dissolution (Gunter et al., 1997; Hitchon et al., 1999). Dissolution or precipitation of carbonates depends upon rock mineralogy and water chemistry. In each case the dissolution and precipitation reactions are a function of thermodynamics and the rates of these reactions are controlled by chemical kinetics.

There have been few studies of CO₂ introduced into a potable aquifer setting. Shallow aquifer conditions are unlike studies done at depth where (1) rocks have generally been flushed by fresh water, (2) CO₂ will be a gas rather than a supercritical fluid, and (3) temperature, pressure, and salinity are lower than in deep reservoirs. While potable waters that are high in CO₂ occur in nature (e.g. the Perrier region of France), these rock-water aquifer systems have had a long period in which to react and equilibrate with CO₂. Hence, they may be an imperfect analogue for short term reactions that could result from accidental leakage of CO₂ into a freshwater aquifer.

3. Laboratory Experiments

BEG researchers conducted laboratory batch experiments to investigate the extent to which injected CO₂ migrating upward into a shallow aquifer could mobilize major and minor ions bound to aquifer host rocks. A series of batch experiments was designed to react diverse aquifer rocks with CO₂ in the medium of water. We selected core samples from the Core Research Center at the BEG with the goal of representing various aquifers present in Texas and throughout the Gulf Coast region. For each reactor 95 g of disaggregated, unwashed rock sample was combined with 500 ml of deionized (DI) water in a wide mouth 500 ml Erlenmeyer flask. Rubber stoppers facilitated airtight placement of inflow and outflow tubes. To minimize the corrosiveness of DI water, sodium chloride (NaCl) was added to approximate natural groundwater activity (~40 ppm Cl⁻). The experiment was split into two periods where in the first period argon (Ar) gas was bubbled through the reactors for two weeks. CO₂ was bubbled through the reactors for a second 2-week period immediately following. When the gas supply was switched from Ar to CO₂ at Day 14, 70 ml of DI water was added to each reactor to replace the water that was removed during the Ar run (dilution factor 1.14). Ten flasks containing samples of aquifer rock and a blank (DI water only) were run simultaneously. The outflow manifold system was open to room atmospheric pressure. During Ar injection 2-ml water samples were taken at 1, 5, 12 hour, 1 day, 2, 4, 7, 10, 12, and 14 day time intervals for ion analysis. Water was sampled on the same schedule during the CO₂ run. After every sampling period, the pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), and conductivity were measured using a multiparameter probe (Hanna Instruments 9828). Cation analysis was done at the University of Texas at Austin Department of Geological Sciences on an Agilent 7500ce Quadrupole ICP-MS. The cation concentrations measured from the reactors with rock samples were subtracted by the measurements of the blank reactor to reduce or eliminate procedural contamination effects. Sodium and chloride were normalized to the amount of NaCl added at the beginning of the experiment and subtracted.

Results show that cation concentrations were generally elevated in the CO₂ experimental run relative to the Ar run. Rapid geochemical response occurred within hours to days after introduction of CO₂ with significant liberation of the cations: Ca, Mg, K, Si, Sr, Mn, Ba, B, Fe, and Al. Concentrations of some cations (e.g. Ca, Mg, Mn, Fe, Sr, Ba) increased over an order of magnitude. Different aquifer rock reactors displayed different magnitudes of increase in cation concentrations. Results of the reactor containing Dockum aquifer rock from Randall County, Texas, U.S.A. are included as an example (Figure 1). Figure 1 shows rapid elevation in concentrations of many of the cations after CO₂ was introduced on day 14. Release rate of all cations decreased towards the end of experiment, where their concentrations increased slowly or remained at a constant level. Good correlation between the concentrations of Ca and Mg suggest dolomite as their source mineral. K and Si may be released from K-feldspar. Two types of cation concentration profiles were recognized after introduction of CO₂ to reactor vessels (1) Type I – concentrations increased rapidly then increased slowly or remained at constant concentrations and (2) Type II – concentrations increased rapidly followed by a gradual decrease. Type I cations include B, Ba, Ca, Co, K, Mg, Mn, Sr and Zn. Type II cations include Al, As, Cs, Cu, Fe, Mo, Ni, Rb, U, and V.

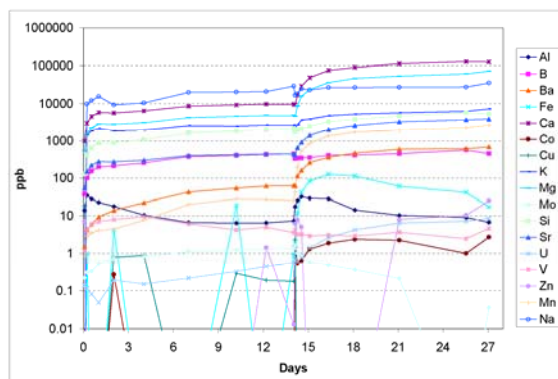


Figure 1. Cation concentrations through the process of experiment. CO₂ was introduced into the system at Day 14.

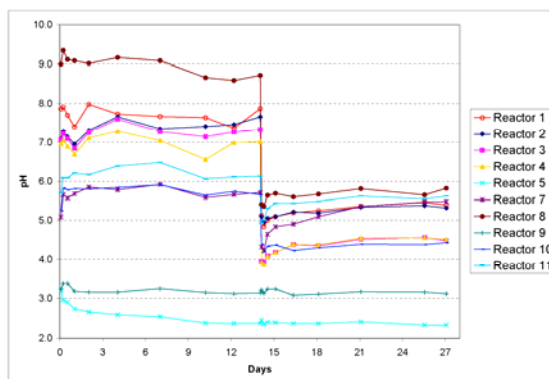


Figure 2. pH through the experiment for all the reactors. CO₂ was introduced into the system at Day 14.

Drop in concentration of Type II cations (e.g. Fe and Al) was unexpected and suggests that cation mobilization reached a maximum concentration followed by resorption and/or reprecipitation. The decline in cation concentrations is tentatively interpreted as a result of reprecipitation or sorption on reactive grain coatings. In the case of stagnant water, resorption suggests that some cation mobilization could be self-mediated by the system. This transience was also detected at the Frio, TX site. The elevation of concentrations of Type II cations, such as, Fe, Al, Mo, U, Cs, Cu, may be a short-term perturbation and therefore a limited risk to water quality. As expected, pH dropped at the start of CO₂ flux for most of the reactors (Figure 2). In most cases, pH rebounded after abrupt decrease at the beginning of CO₂ run, then stayed relatively constant. In general, CO₂ reduced pH values up to 3 units relative to Ar gas. In Reactor 1, for example, pH dropped from over 7.9 to 4.8 within hours after introduction of CO₂, then rebounded and remained at ~5.4. The pH rebound is probably due to mineral buffering, in this case, dissolution of dolomite and, to a lesser extent, potassium feldspar. The experimental results provide initial data for the degree and rate at which cations would be mobilized from aquifer host rocks if they are affected by CO₂ leakage. These data can be used for sensitivity analysis in design of field testing experiments to determine if any of the constituents elevated in the laboratory tests are detectable in groundwater that has or might have come in contact with injectate CO₂. However, significance of elevated minor cations from samples in solution with minimally reactive gas (Ar) shows that the concentrations measured cannot be transferred directly to aquifer conditions. Three hypothesis are proposed to explain overall high cation concentrations (1) DI water with small amount of NaCl added (Cl ~40 ppm) was used in the experiment instead of aquifer water for each sediment, so some dissolution of reactive minerals occurred to reach rock-water equilibrium, (2) disaggregation of the rocks exposed more reactive surfaces than would be exposed in the aquifer setting, and (3) some contamination from the experimental design was noted and factored out, however contamination from sample handling (for example drilling mud introduced during coring or oxidation of core during storage) cannot be removed. If a geometry was created where the same volume of water was charged with excess gas and migrated through many rock volumes, cation concentrations might become quite high. Cation concentrations could also decrease as the reacted groundwater moved away from the CO₂ source and pH was buffered.

4. Field Studies

BEG researchers are currently involved in two field studies in which groundwater monitoring is designed to improve understanding of risk to fresh water from CO₂ injection operations. These studies are located at (1) the SACROC oilfield in Scurry County, Texas, U.S.A. where CO₂ has been injected for EOR since 1972 and (2) the Cranfield unit in Adams County, Mississippi, U.S.A. where CO₂ EOR is currently underway. SACROC offers a great opportunity to study potential impacts to fresh water resources because of the long time span over which to observe effects of engineered CO₂ injection. Since CO₂ EOR began at SACROC, approximately 50% of the 150 million metric tons (MMt) of injected CO₂ has been recovered. The majority of remaining CO₂ is likely trapped in the deep subsurface, but studies to demonstrate CO₂ has been sequestered at SACROC are still in progress. The SACROC oilfield covers a ~90 mi² area in central Scurry County, TX (Figure 3). Geologic units present at the surface range from Permian to Quaternary in age. Two significant water-bearing units crop out at the surface within the study area. The Triassic-age Dockum Fm. (TrD in Figure 3) hosts the Dockum aquifer, which is designated a minor aquifer by the Texas Water Development Board (TWDB). The second significant water-bearing unit is the Ogallala Fm. (P-EOg in Figure 3). This erosional outlier of the Ogallala Fm. is isolated from the Ogallala aquifer of the Texas High Plains, but provides significant fresh water resources in Scurry and surrounding counties. Smaller quantities of fresh groundwater are produced from Permian-age units in eastern portions of the study area.

We have sampled freshwater from wells constructed in Ogallala Fm., Dockum Fm., Permian-age units, and combinations of these geologic units within an ~1,800 mi² area. Depth of wells sampled by BEG and TWDB ranges from 30 to 700 ft. Sampled wells are located over such a large region for several reasons. Limited data on groundwater quality prior to development of oil and gas fields, do not provide adequate background (i.e. prior to CO₂ injection) data against which to compare post-CO₂-injection groundwater quality data. Water wells in the region are completed in numerous different and sometimes multiple geologic units; hence groundwater chemistry is highly variable. In order to determine if freshwater resources over the SACROC oilfield have been impacted by over 35 years of CO₂ injection, we must first define the regional variability in Dockum aquifer groundwater chemistry. In lieu of sampling before and after CO₂ injection, we have sampled inside and outside of SACROC.



Figure 3. Surface geologic units and water wells in vicinity of the SACROC oilfield.

During the SWP SACROC groundwater study BEG researchers have (1) compiled historical groundwater chemistry data from the TWDB online database (196 freshwater wells) and (2) collected multiple samples from 60 freshwater wells, one freshwater spring, and eight production-zone-brine wells. We completed five sampling events between June 2006 and July 2008 within a 1,275 mi² area (Figure 3). Water well sampling methodology included continuous measurement of field chemical parameters (temperature, pH, specific conductivity, and dissolved oxygen) in a flow cell and monitoring of discharge rate. We did not collect groundwater samples until after field chemical parameters stabilized to ensure that samples were from the formation and not stagnant casing-volume-water. Our sampling protocol included field alkalinity titrations in November 2007, March 2008, and July 2008. Laboratory analytes measured in BEG groundwater samples by Los Alamos National Laboratory (LANL) are: Al, Ag, As, B, Ba, Be, Br, Ca, Cd, Cl, CO₃, Co, Cr, Cs, Cu, d¹³C, dD, d¹⁸O, F, Fe, HCO₃, Hg, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, Pb, PO₄, Rb, Sb, Se, Si, Sn, SO₄, Sr, Th, Ti, Tl, U, V, and Zn. Laboratory analytes measured in The University of Texas at Austin Department of Geological Sciences (UT DGS) are dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), methane (CH₄) and CO₂ from headspace gas in selected samples. The chemistry of Dockum groundwater is highly variable. Figure 4 is a Piper plot of BEG Dockum aquifer freshwater samples collected inside and outside of SACROC combined with data from wells completed in underlying zones. Permian well data are from both deeper wells near SACROC and wells located east of SACROC where Permian units crop out at the surface (Figure 4). Samples of produced water (brines) are from SACROC oilfield wells completed at depths between 6,000 and 7,000 ft. There is no distinct grouping of BEG well samples inside versus outside of SACROC (Figure 4). Production zone samples are clearly shown to be sodium-chloride-type waters distinct from most of the BEG samples in all portions of Figure 4.

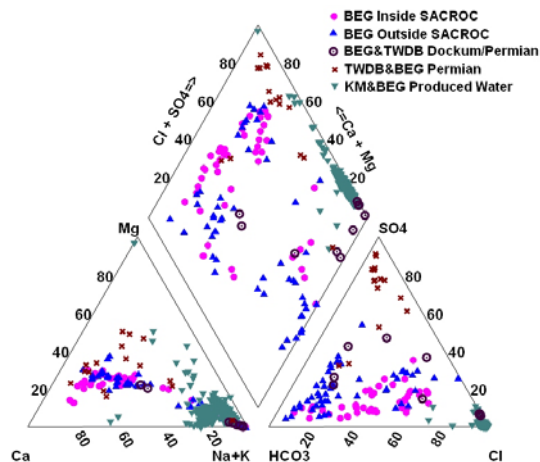


Figure 4. Piper plot of all BEG freshwater samples, BEG and Kinder Morgan produced water.

Trends of major element concentrations suggest mixing of Dockum aquifer groundwater and water with Permian and production zone geochemical signatures. Mixing models from Dr. Changbing Yang (2008, personal communication) at BEG predict that <1 % produced oilfield brine or 12 % Permian water could mix with the lowest TDS BEG Dockum freshwater sample to produce the highest TDS Dockum sample. Several mechanisms can be used to explain such mixing, especially in an oil field that has been operating since the early 1950s.

The main question remains: Has Dockum aquifer water been impacted by the long history of CO₂ injection at SACROC? If conduit flow along leaking well bores is responsible for increased TDS in Dockum water overlying SACROC, we would also expect to see impacts to Dockum water from injectate CO₂. Laboratory experiments and field observations show that pH will decrease and cation concentrations will increase in fluid reservoirs exposed to injected CO₂. Methods for interpreting Dockum groundwater chemistry include spatial plotting of concentration contours. For analytes such as pH, we have valid data spanning pre- and post-injection periods. Pre-1980 pH-data from the TWDB database are shown in Figure 5. Dockum aquifer water pH ranged from ~6.5 to 9.0 in samples collected between 1936 and 1978.

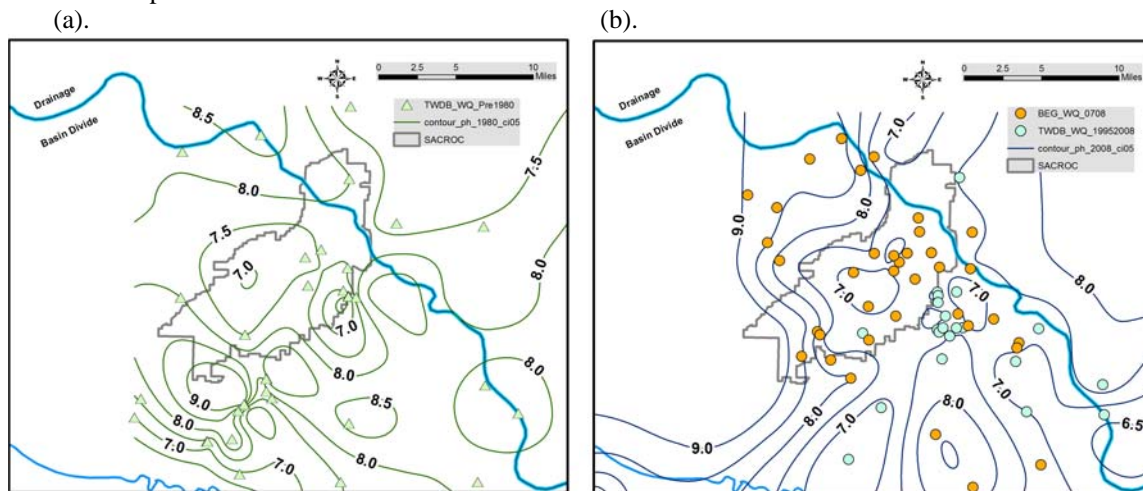


Figure 5. (a) pH values measured in freshwater well samples before 1980 (TWDB). Data points denoted by green triangles. (b) pH values measured in freshwater wells between 1995 (TWDB) and 2008 (BEG&TWDB).

Dockum aquifer pH measured in samples collected from 1995 to 2008, after CO₂ injection had been ongoing for over 20 years, is shown in Figure 5. Careful comparison with pre-1980 contours reveals either no change or a slight increase in pH near SACROC between the two time periods (Figure 5). We would expect to see pH fall if injectate CO₂ had leaked into Dockum freshwater zones or if reservoir brine with lowered pH and increased cation concentrations (as documented at SACROC by Han, 2008) had been displaced upward into Dockum freshwater.

If pH change has been buffered by dissolution of silicate minerals in the Dockum aquifer, cation concentrations would be higher over SACROC. We do not see systematic increases in cation concentrations measured in Dockum aquifer samples inside versus outside of SACROC (figures 5 and 6). However, we are still evaluating the data from the perspective of regional flow paths and reactive transport modeling. Another way to evaluate data from Dockum groundwater samples is to assess degradation of water quality by comparing analyte concentrations to EPA drinking water standards. Data summarized in Table 1 are from BEG samples that were filtered (0.2 to 0.45 µm) in the field. Cation samples were preserved with nitric acid to pH 2. No preservative was added to the anion samples. The percentage of BEG Dockum aquifer samples with analytes exceeding USEPA primary maximum contaminant levels (MCLs) and secondary drinking water standards are highlighted in yellow in Table 1. Without exception, the percentage of samples with analytes in excess of USEPA standards is higher outside than inside of SACROC (Table 1). Arsenic (As) and lead (Pb) are listed as contaminants of particular concern in the July 2008 EPA proposed rule because these constituents might be leached from rocks in GS reservoirs and mobilized to impact USDWs. Of the 9.8 percent of wells with As levels above MCLs, only 1.6 percent of these are inside SACROC (Table 1). Only ~12 percent of the filtered BEG Dockum samples had Pb levels above a detection limit of 0.002 mg/L. Forty two percent of these samples are from wells inside versus 58% outside of SACROC.

Table 1. Comparison of EPA drinking water standards with BEG Dockum aquifer well data.

Analyte	EPA/TCEQ Primary Drinking Water MCL (mg/L)	BEG Wells Exceeding EPA Standards	BEG Wells Exceeding EPA Standards - Inside SACROC	BEG Wells Exceeding EPA Standards - Outside SACROC
<u>Primary Maximum Contaminant Level (MCL)</u>				
Arsenic (As)	0.01	9.8 %	1.6 %	8.2 %
Cadmium (Cd)	0.005	1.6 %	0.0 %	1.6 %
Fluoride (F ⁻)	0.4	4.9 %	1.6 %	3.3 %
Nitrate (NO ₃ -N)	10	13.1 %	4.9 %	8.2 %
Selenium (Se)	0.05	4.9 %	1.6 %	3.3 %
<u>Secondary Drinking Water Standard</u>				
Aluminium (Al)	0.05	34.4 %	13.1 %	21.3 %
Chloride (Cl ⁻)	250	32.8 %	14.8 %	18.0 %
Fluoride (F ⁻)	0.2	37.7 %	14.7 %	23.0 %
Manganese (Mn)	0.05	14.7 %	4.9 %	9.8 %
Sulfate (SO ₄ ²⁻)	250	26.2 %	1.6 %	24.6 %
Total Dissolved Solids (TDS)	1000	50.8 %	18.0 %	32.8 %

BEG researchers are studying stable carbon isotopes of fresh water, produced water, injectate CO₂, and plant matter, which forms the substrate for microbial oxidation of CO₂. Solid carbonate phase is also important but analytical results are not yet available from LANL. Potential contributions to the carbon isotope signature include mixing with Permian and produced water, microbially-produced CO₂, carbonated dissolution, and injectate CO₂. A plot of carbon isotope ratios versus dissolved inorganic carbon (DIC) shows an increase in light carbon with increasing DIC. This is consistent with input from microbial CO₂ but does not rule out the presence of injectate CO₂. Further studies are in progress at BEG.

5. Summary

Laboratory experiments and field observations show that pH will decrease and cation concentrations will increase in fluid reservoirs exposed to injected CO₂. This has been shown to be true in the 6,000 to 7,000 ft deep injection/production zones of the SACROC oilfield (Han, 2008). Underground sources of drinking water overlying SACROC are contained within multiple stratigraphic horizons of the Dockum aquifer. Chemical constituents measured in samples of Dockum groundwater suggest minor mixing with more saline (higher TDS) Permian water or co-produced oilfield brines. However, this does not imply that CO₂ injected for EOR at SACROC has mixed with Dockum groundwater. Analysis of BEG/LANL stable carbon isotopic data to trace various sources of CO₂ in the subsurface above SACROC is in progress. Dockum aquifer chemical concentrations inside of SACROC fall within the range of TWDB groundwater chemical analyses in samples taken from a multi-county region surrounding SACROC. We do not see evidence of As or Pb having been mobilized from injection zones at SACROC into overlying USDWs (Dockum aquifer zones). There are Dockum wells with chemical constituents in excess of EPA drinking water standards within our study area. However, a larger percentage of these wells are located **outside** of the SACROC oilfield. The main conclusion is that no widespread degradation of water quality exists inside the SACROC oilfield as a result of CO₂-injection. Work is in progress to determine if CO₂ injection at SACROC is changing regional Dockum aquifer groundwater flow patterns.

6. Acknowledgements

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