

SACROC Groundwater Study Final Report

Executive Summary

The Department of Energy National Energy Technology Laboratory (NETL) funded the Southwest Regional Carbon Sequestration Partnership (SWP) for Phase II research at the Scurry Area Canyon Reef Operators Committee (SACROC) oilfield on the eastern edge of the Permian Basin from 2006 through 2010. Researchers at the Gulf Coast Carbon Center (GCCC) (www.gulfcoastcarboncenter.org) at the Bureau of Economic Geology, University of Texas at Austin managed SWP research efforts at SACROC and subcontracted with New Mexico Tech to perform a field-based-groundwater study described in this report. Injection of CO₂ for enhanced oil recovery (EOR) has been ongoing at SACROC since 1972. The idea conceived by Susan Hovorka, PI for the GCCC, and GCCC industrial sponsors (Michael Hirl, formerly with Kinder Morgan, and Charles Christopher, retired from BP) was that if CO₂ injection into the deep subsurface is going to degrade shallow drinking water resources, SACROC is the best place to look.

Monitoring groundwater resources over CO₂ geologic sequestration (GS) sites is needed to protect potable water supplies and insure that CO₂ is adequately sequestered with respect to the biosphere. For these reasons it is good to study worst-case-scenarios where CO₂ might be directly released into drinking water, as is currently taking place at other NETL Regional Carbon Sequestration Partnership (RCSP) project sites. However, the value of the SACROC groundwater study lies in the long history of CO₂ injection in an oilfield with thousands of active and abandoned wells. According to our industrial partner, Kinder Morgan (KM), over 175 million metric tons of CO₂, primarily from a natural source in Colorado, were injected at SACROC for EOR between 1972 and 2010. **The fact that the quality of shallow drinking water over SACROC has not been impacted by CO₂ injection is strong evidence that it is possible to safely sequester CO₂ in deep subsurface reservoirs.**

GCCC performed groundwater monitoring [chemical sampling (113 samples from 34 domestic/stock, 12 abandoned, and 8 irrigation wells and 1 spring) and water level measurement] within a ~1,000-mi² area between June 2006 and November 2008. We augmented the datasets using an online historical database from the Texas Water Development Board (TWDB). The primary source of drinking water in the SACROC area is the Triassic-age Dockum aquifer. The Dockum is a heterogeneous hydrogeologic unit composed of multiple strata not previously recognized as isolated water-bearing zones within the study area.

Dockum aquifer wells range from ~50-500 ft depth; water samples contain ~400-2,300 mg/L total dissolved solids (TDS). The oil production/CO₂-injection zone lies at 6,000-7,000 ft depth and contains brine with 50,000-200,000 mg/L TDS. Intermediate depth zones, above the Wolfcamp Formation low-permeability seal, are composed of gypsum-bearing, Permian-age strata. BEG researchers analyzed chemical trends of major elements dissolved in groundwater. Distribution of anions shows that Dockum waters outside of SACROC trend toward Permian water composition (CaSO₄); those inside SACROC trend toward produced water (NaCl). **Otherwise, there are no significant differences between Dockum groundwater inside versus outside of SACROC**, and all GCCC-samples fall within regional variation as defined by TWDB

data. Mixing of these multiple sources of groundwater controls groundwater chemistry through cation exchange and a water-rock interaction called dedolomitization (incongruent dissolution of dolomite and precipitation of calcite).

A widely posited hypothesis is that carbonate parameters alone can be used to monitor groundwater quality over a GS site. This is not the case for the Dockum aquifer and likely many others around the world. Dedolomitization caused by mixing with Permian water, and not calcite dissolution, is the geochemical process that dominates the Dockum groundwater system. In an analysis of calcium (Ca^{2+}) versus bicarbonate (HCO_3^-), GCCC and TWDB data fit modeled curves for dedolomitization, and do not follow a calcite dissolution trend. Instead, data follow increased dedolomitization trends toward higher Ca^{2+} and lower HCO_3^- , but migrate toward higher PCO_2 values with increased water-rock interaction. The increase in PCO_2 is explained through stable carbon isotope ($\delta^{13}\text{C}$) modeling (using PHREEQC code combined with mass balance equations) to be a result of dedolomitization and microbial degradation of organic material.

It is widely recognized that introduction of CO_2 into groundwater will mobilize ions and increase total dissolved solids (TDS). However, our results do not support the hypothesis that contamination of aquifers by increased concentrations of arsenic (As), lead (Pb), or zinc (Zn) will be a likely result of CO_2 GS. Analysis of GCCC and TWDB data over time for TDS, As, and Zn indicate that these parameters have not increased over time or are not significantly higher in wells inside versus outside of SACROC. Pb was measured above a detection limit of 0.0002 mg/L in 11 of the 59 wells sampled by GCCC. Of these 11, six are outside and five are inside of SACROC. The range of values of Pb detected in wells is between 0.0002-0.00105 mg/L, which is below the drinking water standard (DWS) of 0.01 mg/L. Interestingly, most of the Pb detections are from samples collected in July 2007, with repeat results from the same wells at other sampling trips being below detection limits.

More wells outside of than inside of SACROC had detections of analyte concentrations in excess of DWS values. Exceptions to this are (1) NO_3^- concentrations, which we think are higher over SACROC from agriculture, and (2) Cl^- concentrations, which we think comes from past oilfield practices over SACROC (i.e. brine evaporation pits that used to be maintained on the surface, or leaking brine disposal pipelines and wells).

Introduction

Monitoring groundwater resources above geologic carbon sequestration reservoirs is proposed for ensuring that potable water supplies remain protected and also for establishing that CO_2 is adequately sequestered with respect to the biosphere. As extensive application of geologic CO_2 sequestration is considered worldwide, it is important to determine the potential for widespread usage of shallow aquifer geochemistry for CO_2 storage evaluation and to determine the parameters best-suited for monitoring these resources.

In a hypothesized scenario of leakage from a CO_2 injection reservoir, CO_2 may rise buoyantly from the injection zone through breaches in sealing formations (i.e. faults) (Chang et al., 2009; Zhang et al., 2009), or leaky plugged and abandoned wells (Gasda et al., 2009; Pan et al., 2009)

or CO₂ may be carried upward in CO₂-charged brine that is displaced by reservoir over pressuring (Bachu and Bennion, 2009; Nicot, 2008). In any case, CO₂ moving upward from a storage reservoir may eventually intersect and interact geochemically with fresh water aquifers, rendering these environments as areas to monitor for leakage detection.

The success of using shallow groundwater geochemistry as a tool for CO₂ storage evaluation depends upon the ability to identify one or more geochemical parameters sensitive enough to provide a recognizable geochemical shift upon addition of exogenous CO₂ to the aquifer. This requires a shift that is larger than background variability and is therefore detectable as an indicator of change. Widespread application of a standard method to a variety of geologic sequestration (GS) locations also necessitates that the type and magnitude of geochemical shift is similar or at least predictable in any geochemical environment even though hydrochemical processes and mineralogies differ widely among aquifers.

The current position of many researchers is that the predictable consequence of CO₂ input into a dilute aquifer is calcite dissolution leading to: 1) decrease in pH; 2) increase in dissolved inorganic carbon (DIC) as alkalinity, H₂CO₃, or HCO₃⁻; 3) increase in Ca²⁺ and/or Mg²⁺ from dissolution of common carbonate minerals, calcite and dolomite; and 4) eventual mobilization of metals from mineral dissolution and desorption reactions. Therefore, a popular suggestion is that carbonate parameters (DIC, pH, and Ca²⁺) are suitable for relatively early detection of exogenous input of CO₂ into groundwater resources. The potential for using carbonate parameters to monitor aquifers at carbon sequestration sites will therefore depend on the reactivity of aquifer minerals to CO₂. Because carbonates are kinetically more favorable to reaction than silicates, geochemical shifts from CO₂ input can result even though silicates may predominate volumetrically (Blum et al., 1998).

Hypotheses have emerged from studies that incorporate a broad number of approaches from theoretical modeling using compilations of aquifer databases (Apps et al., 2009; Carroll et al., 2009; Wang and Jaffe, 2004; Wilkin and Digiulio, 2010; Zheng et al., 2009) to laboratory batch experiments (Lu et al., 2010; Yang et al., 2010) to controlled field experiments (Assayag et al., 2009; Kharaka et al., 2010). While these approaches all yield useful information for assessing the geochemical outcomes of increased CO₂ in freshwater aquifers and their effects on drinking water quality, they exclude the dynamic interplay and effects of local hydrologic conditions on geochemistry.

For example, we know of few, if any researchers who have included the possibility of dedolomitization in their assessments. This well-documented process (also known as incongruent dissolution) occurs under a variety of environmental conditions that produce mixing of dilute and concentrated Ca-rich waters in the presence of calcite and dolomite (Appelo and Postma, 2007; Back et al., 1983; Back et al., 1979; Back and Baedeker, 1989; Bischoff et al., 1994; Hanshaw and Back, 1985; Pacheco and Szocs, 2006; Plummer and Back, 1980). Input of calcium ions via mixing with CaSO₄-type waters has been documented to occur either through dissolution of interbedded gypsum (Cardenal et al., 1994; Plummer et al., 1990), the incorporation of CaSO₄ waters into limestone aquifers resulting from groundwater pumping (Appelo and Postma, 2007; Lopez-Chicano et al., 2001), or by introducing domestic leachates from fertilizers (Pacheco and Szocs, 2006).

Introduction of Ca^{2+} into an aquifer can also result from input of Na^+ -rich waters accompanied by cation exchange. For example, cation exchange driven by mixing has been documented at the freshwater/saltwater interface in the Netherlands and in the Nile delta (Appelo and Postma, 2007). In the SACROC area of this study, as well as throughout Texas and many United States oil producing regions, significant volumes (on the order of millions of tonnes/year) of NaCl brines co-produced with oil from the 1940s through the 1960s were disposed into unlined surface pits. In one example (Burnitt et al., 1963) from 1961, more than 9 million tonnes of co-produced saltwater were disposed into unlined surface pits located directly on outcrops of the Ogallala Formation, which contains a major aquifer on the Texas High Plains. The result was direct contamination of large volumes (on the order of 100's of millions of liters) of fresh groundwater (Ludwig, 1972). Large contaminant plumes are predicted to persist for hundreds of years adding slugs of salts to aquifers with each surface recharge event (Fryberger, 1972; Pettyjohn, 1982).

Regional Hydrogeology

The SACROC oilfield in Scurry County, near Snyder, Texas, lies on the eastern edge of the Permian Basin in western Texas (Fig. 1). Oil production is from the Pennsylvanian/Permian Cisco and Canyon Reef formations located in the Horseshoe Atoll, one of the largest subsurface reefs in the world at 280 km long and 2000 m depth (Anderson et al., 1954; Olien and Olien, 1982). These late Pennsylvanian/early Permian shelf carbonates are overlain by salt, anhydrite, dolomite, limestone and rebeds deposited in a variety of environments ranging from subtidal to supratidal (Gustavson, 1986). The overlying Triassic Dockum Group, contains the potable water source that is investigated in this study.

Although not used as a major water resource, the Dockum is locally important, serving as the source for local public water supply, irrigation for farming, livestock management, and oil-field operations (Bradley and Kalaswad, 2003). Groundwater in the Dockum Group is fresh to brackish (total dissolved solids < 5,000 mg/L) and is locally impacted by dissolution of evaporite deposits in underlying Permian formations (Bradley and Kalaswad, 2003; Dutton, 1989). This impact is due to interaction between two regional aquifers in the Southern High Plains and Rolling Plains. These aquifers include: 1) the Southern High Plains aquifer (SHP) residing primarily in the Tertiary sediments of the Ogallala formation, but also including the Dockum group down to the evaporite-bearing Permian Quartermaster Formation and Whitehorse Group (Richter and Kreitler, 1986); and, 2) the more regionally extensive underlying Paleozoic “deep basin brine” aquifer (DBB) that is separated from the SHP by the Permian layers which comprise an evaporite aquitard of halite, anhydrite, carbonate and mudstone (Bassett et al., 1981; Jorgensen et al., 1988).

Flow within both aquifers is predominantly eastward (McNeal, 1965), with discharge points for the DBB east of the Texas Panhandle in north-central Texas and Oklahoma (Jorgensen et al.,

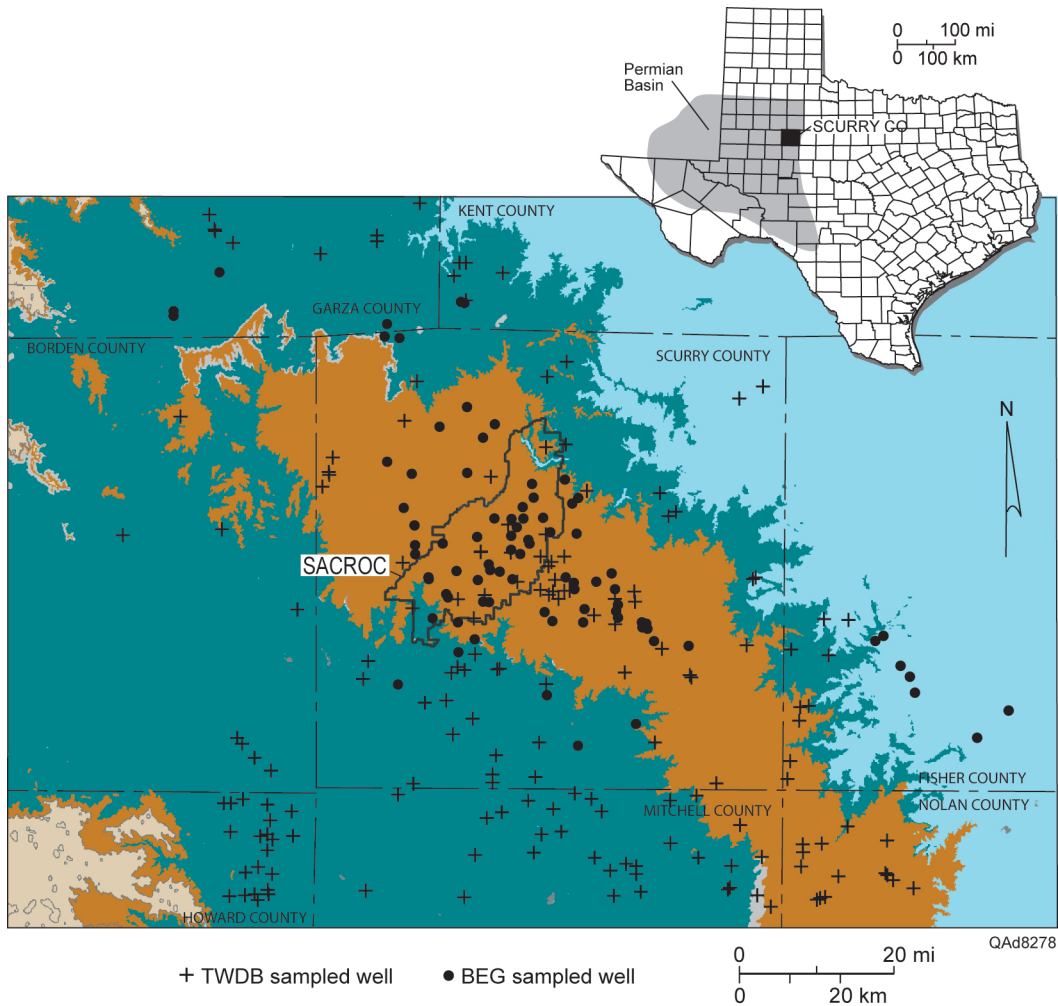


Figure 1. Location of the SACROC oil field in Scurry county, Texas on the eastern edge of the Permian Basin. The oil field lies on a remnant of Ogallala Formation (Eo) surrounded by outcrops of the Dockum Formation (TrD) which houses the aquifer of interest. Undifferentiated Permian formations (P) outcrop to the east. Sample locations are shown.

1988) and discharge points for the SHP aquifer just east in the Rolling Plains, near the SACROC study area. Potentiometric pressures of the Dockum group aquifer in some areas indicate the potential for downward flow into the upper portion of the evaporite aquitard (Fink, 1963) causing a zone of dissolution referred to as a “salt dissolution zone.” Numerical models by Simpkins and Fogg (1982) and Gustavson et al. (1980) show that meteoric groundwater percolating upward into the up-dip Permian halite deposits moves eastward along highly transmissive dolomite and gypsum layers, discharging in topographically low areas. These mixed waters are transported through fractures from the dissolution zone to the surface, interacting with fresh water along the way (Fink, 1963; Jorgensen et al., 1988). Salt springs attributed to dissolution of underlying Permian sequences of gypsum, halite, and dolomite are well-documented north of Scurry County in Garza, Kent, and Stonewall Counties (Stevens, 1974; Richter and Kreitler, 1986; Richter et al., 1990).

Methods of SACROC groundwater study

Because data on groundwater quality prior to CO₂ injection at SACROC are spatially and temporally limited, there is not a good “background” dataset against which to compare post-CO₂-injection groundwater quality. For this reason, and to understand why Dockum groundwater is chemically heterogeneous, our study covered ~1,000-mi²). In lieu of sampling before and after CO₂ injection, BEG sampled both inside and outside SACROC during two consecutive years to assess spatial variation in groundwater chemistry.

During the SWP SACROC groundwater study BEG researchers:

- compiled historical (dating back to 1936) to recent (2008) groundwater chemistry data for eight counties from the TWDB online database (TWDB, 2009),
- collected multiple freshwater samples from 60 private water supply wells (113 samples) and one spring (1 sample), and brine from eight production/injection wells (10 samples);
- compiled chemical data from SACROC production/injection zone brine analyses;
- conducted a study of shallow subsurface stratigraphy,
- measured water levels to construct potentiometric surface maps and identify groundwater flow paths in the Dockum aquifer
- assessed water quality of potable drinking water zones overlying SACROC
- performed geochemical modeling to identify controlling processes and interpretation of groundwater systems overlying SACROC.

BEG researchers completed six water quality sampling and water level monitoring trips between June 2006 and November 2008. 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. To ensure that samples were from the formation and not stagnant casing-volume-water, we did not collect groundwater samples until after field chemical parameters stabilized. We performed alkalinity titrations in the field using filtered, unpreserved water samples. Other sampling protocol included: (1) field filtering and acid preservation of cation samples and (2) storage of all samples at temperature below 4°C immediately after sampling and during shipping.

Laboratory analytes measured in BEG groundwater samples by LANL are: Al, Ag, As, B, Ba, Be, Br, Ca, Cd, Cl, CO₃, Co, Cr, Cs, Cu, δ¹³C, dD, δ¹⁸O, F, Fe, HCO₃, Hg, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, Pb, PCO₂, PO₄, Rb, Sb, Se, Si, Sn, SO₄, Sr, TDS, Th, Ti, Tl, U, V, and Zn. Laboratory analytes measured by 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.

Analysis of the chemical controls on SACROC groundwater chemistry has been a complex and lengthy process during which we evaluated multiple processes prior to conducting extensive modeling. These evaluated processes include:

- Systematic changes in major element and isotopic chemistry along flow paths away from or across SACROC
- Systematic changes in groundwater chemistry with depth

- pH trends inside vs. outside of SACROC
- chemical trends related to stratigraphic unit
- variation of calcite and dolomite saturation indices with other geochemical parameters
- variations in all other analytes inside versus outside SACROC
- Chemical trends with Ca, Na, Cl, SO₄, and
- Oxygen and deuterium trends.

BEG researchers conducted multiple phases of geochemical modeling that can be summarized as follows:

1. Modeling of major ions shows mixing (Permian, Dockum, Ogallala, and produced waters), cation exchange, and dedolomitization are the major geochemical processes.
 - a. Three samples “representative” of end members are used; however, the chemical variability of the samples precludes choosing discrete end members. This model only gives an idea of the basic carbonate geochemical processes.
2. The carbonate system is dominated by dedolomitization, not calcite dissolution, and is a consequence of mixing, not CO₂ input.
 - a. Assume that more “evolved” samples have higher PCO₂ due to either
 - i. degassing during dedolomitization in a closed system
 - ii. input of exogenous CO₂
 - iii. input of microbial CO₂
3. Carbon isotope variations result mostly from dedolomitization reactions which are slightly degassing.
 - a. Major assumptions are in the end member carbon isotope variability and the values used for modeling. Calcite and dolomite are not distinguished. The same ¹³C is used for calcite as for dolomite. Also, average values are used for injectate and microbial CO₂. Variability in these values is not shown in the model.

Results of SACROC Groundwater Study

Ranges and median values of 40 chemical analytes, total dissolved solids (TDS), and well depths for BEG freshwater samples are shown in Table 1. This table includes results from all 60 BEG-sampled water wells in Fisher, Garza, Kent, and Scurry counties. Analytes of particular concern in proposed EPA rules for geologic sequestration are pH, arsenic, lead, mercury.

GCCC laboratory tests and results from other studies show that pH will decrease and dissolved solids (TDS) will increase when CO₂ concentration in groundwater is increased. However, our analysis of TWDB and BEG pH data over time (1956-2008) does not reveal anomalous pH or TDS values associated with SACROC (figures 2 through 5). Plots of other analytes show similar consistencies in time and space.

Table 1. Chemical analyte ranges and median values for 113 BEG freshwater samples collected from private wells in Fisher, Garza, Kent, and Scurry counties.

Analyte	range (mg/L)	median (mg/L)	# nd
Silver (Ag)	all nd	na	113
Aluminium (Al)	0.0005 - 0.2439	0.01	25
Arsenic (As)	0.0004 - 0.0278	0.004	6
Boron (B)	0.03 - 2.17	0.26	0
Barium (Ba)	0.01 - 0.54	0.07	1
Berilium (Be)	all nd	na	113
Bromide (Br)	0.05 - 3.64	0.46	2
Calcium (Ca)	1.28 - 596.56	77.96	0
Cadmium (Cd)	0.87	0.87	112
Chloride (Cl)	8.43 - 1129.08	115.68	0
Chromium (Cr)	0.001 - 0.029	0.002	49
Copper (Cu)	0.0006 - 0.0238	0.0029	21
Cobalt (Co)	0.001	0.001	112
Fluoride (F)	0.586 - 7.750	1.598	3
Iron (Fe)	0.008 - 0.277	0.028	34
Bicarbonate (HCO ₃)	19.86 - 795.69	312.00	0
Mercury (Hg)	0.0001 - 0.0004	0.0001	102
Potassium (K)	0.63 - 10.72	3.44	0
Lithium (Li)	0.021 - 0.199	0.070	1
Magnesium (Mg)	0.43 - 396.72	21.17	0
Manganese (Mn)	0.001 - 0.677	0.008	30
Molybdenum (Mo)	0.001 - 0.025	0.004	20
Sodium (Na)	7.38 - 985.88	87.83	0
Nickel (Ni)	0.0008 - 0.1800	0.0041	19
Nitrate (NO ₃)	0.07 - 206.34	8.10	7
Lead (Pb)	0.0001 - 0.0123	0.0006	99
Phosphate (PO ₄)	0.17 - 0.25	0.21	111
Rubidium (Rb)	0.001 - 0.004	0.001	55
Antimony (Sb)	all nd	na	113
Selenium (Se)	0.001 - 0.082	0.005	17
Silica (Si)	2.98 - 29.63	21.27	0
Sulfate (SO ₄)	11.51 - 2931.02	97.37	0
Strontium (Sr)	0.05 - 14.58	1.34	0
Thorium (Th)	all nd	na	113
Titanium (Ti)	0.003 - 0.007	0.003	110
Thallium (Tl)	all nd	na	113
Uranium (U)	0.0002 - 0.0624	0.0067	7
Vanadium (V)	0.001 - 0.140	0.020	28
Zinc (Zn)	0.003 - 0.476	0.018	7
pH	6.73 - 8.63	7.23	0
TDS	358 - 6194	825	0
well depth (ft bgl)	30 - 500	na	na

nd - below analytical detection limit; na - not applicable

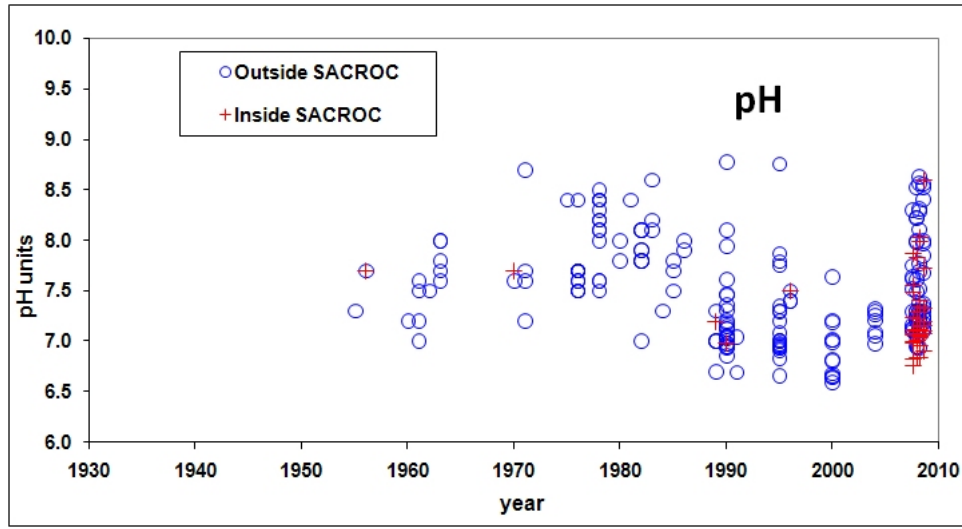


Figure 2. TWDB (1956-2008) and BEG (2007-2008) pH data from Borden, Fisher, Howard, Kent, Mitchell, Nolan, and Scurry counties, TX

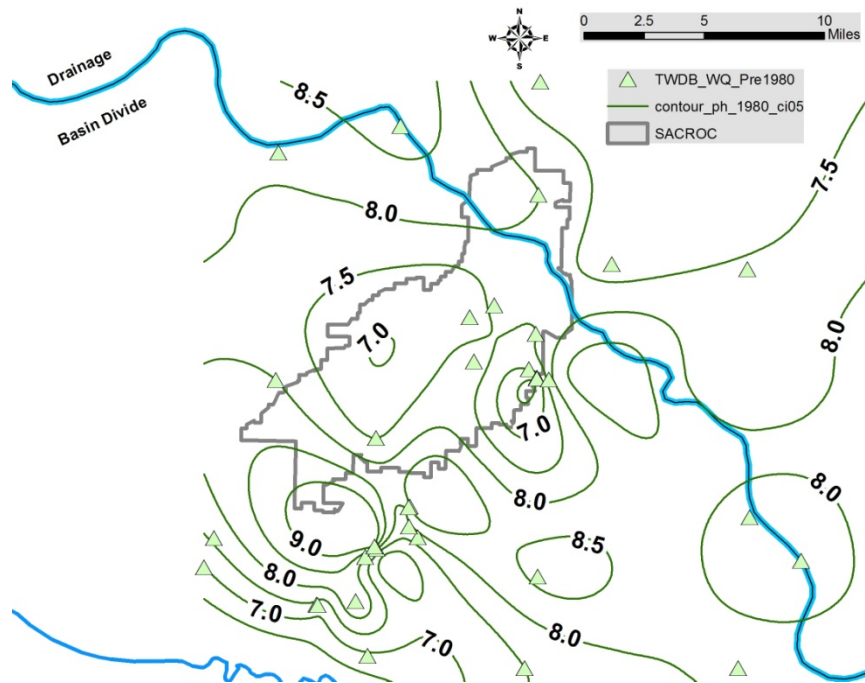


Figure 3. Contours of pH measured by TWDB in Scurry County between 1956 and 1980. Contour interval = 0.5 pH units.

The pH measured in Dockum aquifer samples collected from 1995 through 2008, after CO₂ injection had been ongoing for over 20 years, is shown in figure 4. Careful comparison with pre-1980 contours reveals either no change or even a slight increase in pH near SACROC between the two time periods (figures 3 and 4). We would expect to see the reverse trend in pH if either (1) injectate CO₂ had leaked into Dockum freshwater zones or (2) reservoir brine with

lowered pH and increased cation concentrations had been displaced upward into Dockum freshwater zones.

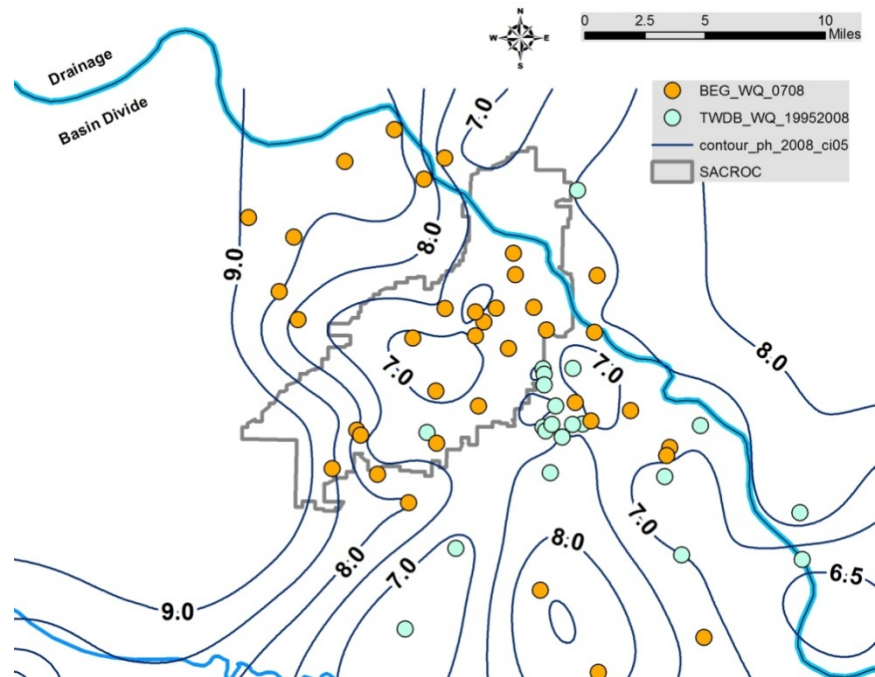


Figure 4. Contours of pH measured by BEG and TWDB in Scurry County between 1995 and 2008. Contour interval = 0.5 pH units.

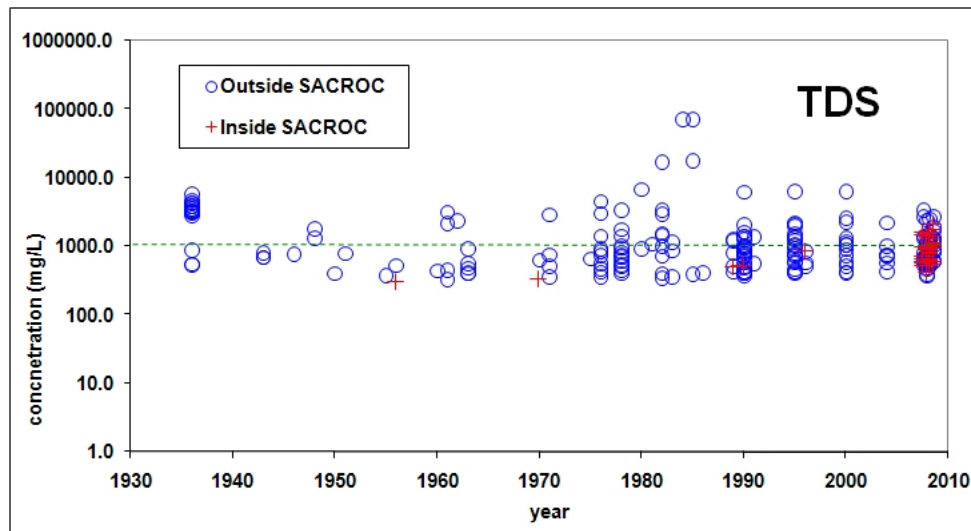


Figure 5. TWDB (1936-2008) and BEG (2007-2008) total dissolved solids (TDS) data from Borden, Fisher, Howard, Kent, Mitchell, Nolan, and Scurry counties, TX

Water wells in the region are completed in numerous different and sometimes multiple geologic units. The TWDB is a State agency that studies groundwater resources in Texas. They have delineated major and minor aquifers throughout Texas based on estimates of groundwater quantity and quality. One of the minor aquifers of Texas, the Dockum, underlies the SACROC oilfield in Scurry County and surrounding areas. The majority of water wells in Scurry Co. are classified as Dockum wells by the TWDB. During the BEG study of groundwater resources in

the vicinity of SACROC we identified large variations in well depth, static water level, and water chemistry of freshwater wells. The base of fresh water is at approximately 500 ft below ground surface at the base of the Triassic Dockum Formation. The SACROC production/injection zones are in the Pennsylvanian/Perman age Canyon and Cisco formations at approximately 6,500 ft below surface (table 2).

Table 2. Stratigraphic units in the subsurface below the SACROC oilfield (multiple sources for stratigraphic nomenclature)

SYSTEM	SERIES	GROUP	FORMATION	Alt. FORMATION	WATER-BEARING UNIT	
Quaternary			Alluvium			
			Seymour		Seymour	
Tertiary			Ogallala Fm.		Ogallala Aquifer	
Triassic		Dockum	Cooper Canyon		Dockum Aquifer	
			Trujillo			
			Tecovas Santa Rosa			
	Ochoan	Quartermaster	Rustler		Rustler Aquifer (W TX)	
			Salado			
	Guadalupian	Whitehorse	Tansill		Whitehorse	
			Artesia (New Mexico)	Yates		
			Capitan Reef (Midland Basin)	Seven Rivers Queen Grayberg		
			Pease River			Blaine Aquifer (Panhandle)
		Cherry Canyon Brushy Canyon	San Andres San Angelo	Blaine Glorieta		
	Leonardian	Clear Fork	Choza			
				Vale Arroyo	Upper Sprayberry Lower Sprayberry	
			Leuders	Clyde		
			Talpa			
			Grape Creek	Bell Plains		
Permian		Wichita-Albany	Jagger Bend-Valera			
			Elm Creek	Admiral		
			Admiral Coleman Junction			
	Wolfcampian		Santa Ana Branch Shale	Putnam		
		Cisco	Sedwick Ls.			
			Moran			
			Harpersville Thrifty Graham			
Pennsylvanian		Canyon Group	Colony Creek			
			Ranger			
			Placid			
			Winchell			
		Wolf Mtn.				
		Palo Pinto				
			Strawn Group	Mineral Wells Brazos River Mingus Grindstone Creek Lazy Bend		

BEG sampled freshwater from wells constructed in the Ogallala Formation, Dockum Formation, Permian-age units, and combinations of these geologic units. By plotting depth of water wells and depth to top and bottom of the Dockum Santa Rosa (figure 6), we classified wells by stratigraphic unit in which they are completed. Figure 7 shows BEG wells classified by geologic formation in which they are completed. We are currently evaluating groundwater chemistry trends by grouping data according to stratigraphic unit in which they are completed.

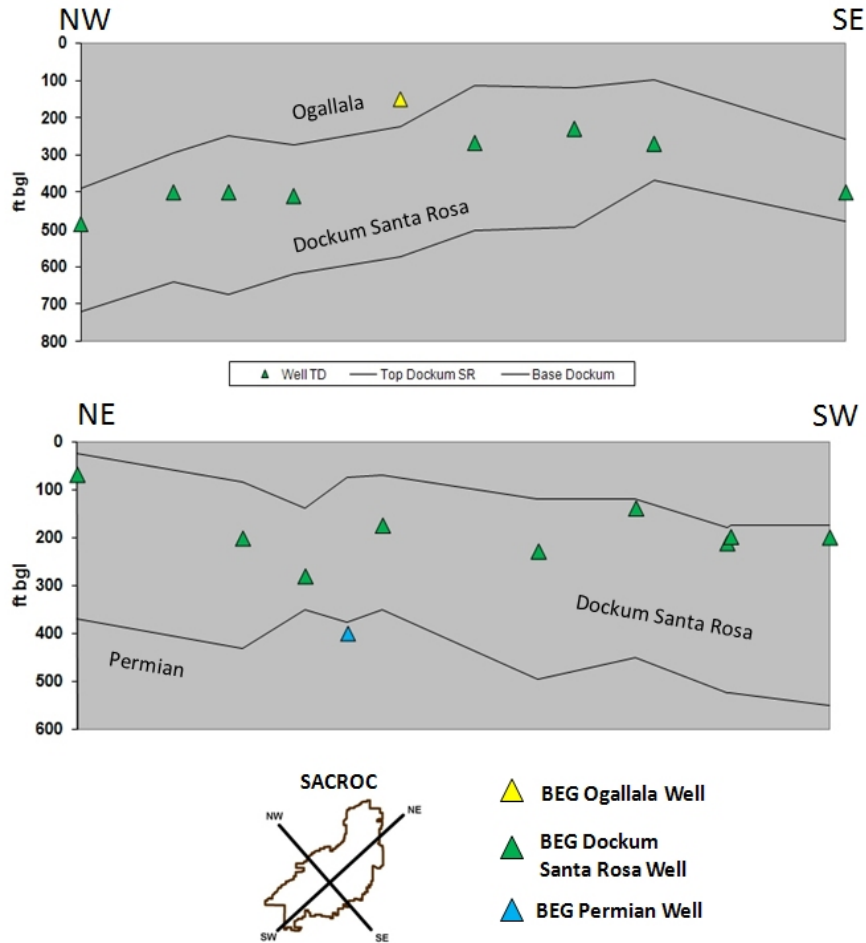


Figure 6. Scaled cross sections of selected BEG-sampled wells relative to top and bottom of Dockum Santa Rosa subunit of Dockum aquifer.

Geologic units present at the surface within our study area 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 Formation (Fm.) (TrD in Figure 7) hosts the Dockum aquifer. The second significant water-bearing unit is the Ogallala Fm. (P-EOg in Figure 7). This erosional outlier of the Ogallala Fm. is isolated from the Ogallala aquifer of the Texas High Plains but provides significant freshwater resources in Scurry and surrounding counties. Smaller quantities of fresh groundwater are produced from Permian-age units in the east parts of the study area (Figure 7).

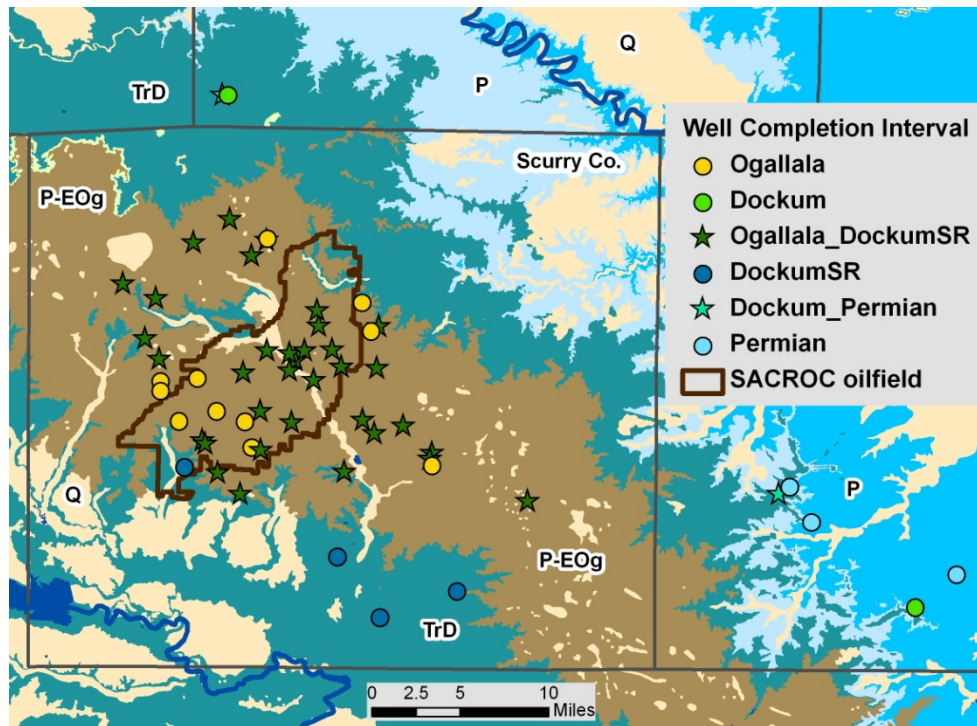


Figure 7. Locations of wells monitored for SWP SACROC groundwater study superimposed on surface geologic units. Geologic unit abbreviations: Q- undifferentiated Quaternary units; P-EOg – Paleocene-Eocene Ogallala Fm.; TrD – Triassic Dockum Fm.; P – undifferentiated Permian units.

Chemistry of Dockum aquifer groundwater is highly heterogeneous. The chemistry of Dockum aquifer groundwater varies greatly because (1) the Dockum Formation is heterogeneous, (2) the history of oil and gas activity in the region is long, and (3) wells designated as Dockum aquifer by TWDB are completed in different stratigraphic intervals. Wells completed within the Ogallala outcrop are designated by TWDB as Dockum aquifer wells even though not all of them extend into the underlying Dockum Formation, which is subdivided into different depositional units with depth (McGowan et. al., 1979), not all of which are hydraulically connected. A few Dockum aquifer wells penetrate multiple Dockum subunits and extend into underlying Permian-age strata. Ranges of analytes measured in all freshwater wells sampled by BEG

A Piper diagram is a graphical display used to show variations in large groundwater chemistry datasets. Milliequivalent percentages of major cations (Ca, K, Mg, and Na) and anions (Cl, HCO₃, and SO₄) are plotted on trilinear diagrams, and combined values are projected onto a central quadrilateral plot. A Piper diagram of TWDB database samples from Dockum aquifer wells in Scurry and immediately surrounding counties (figure 8) shows tremendous variation in chemical composition, especially for a single aquifer. Most of the TWDB historical samples are from areas outside SACROC, but there is no clear distinction between samples collected inside versus outside the SACROC oil field (figure 9).

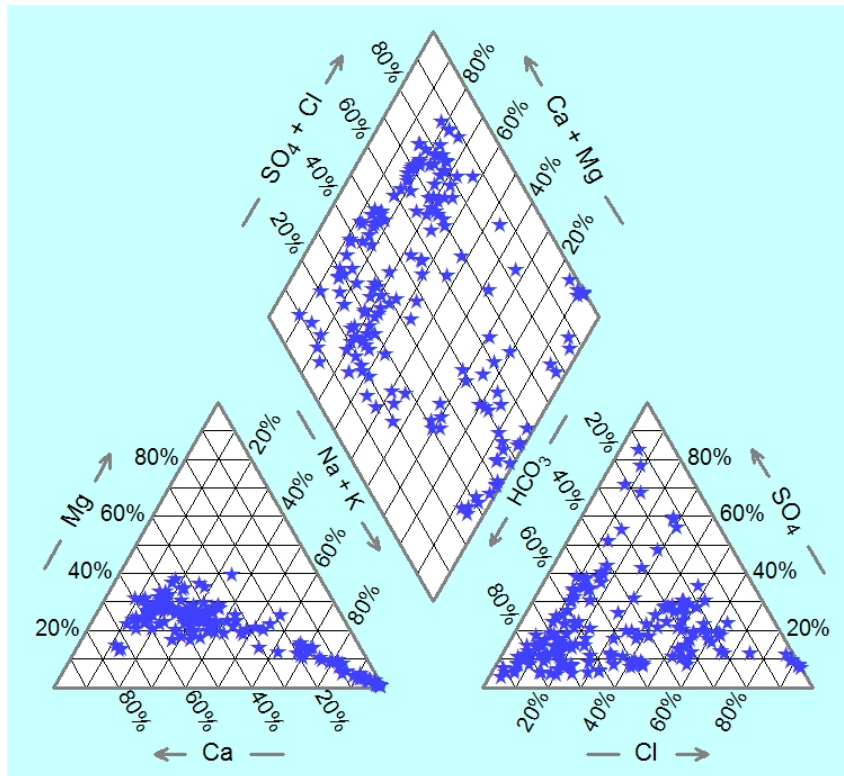


Figure 8. Piper diagram showing large variation in water chemistry for BEG and TWDB wells.

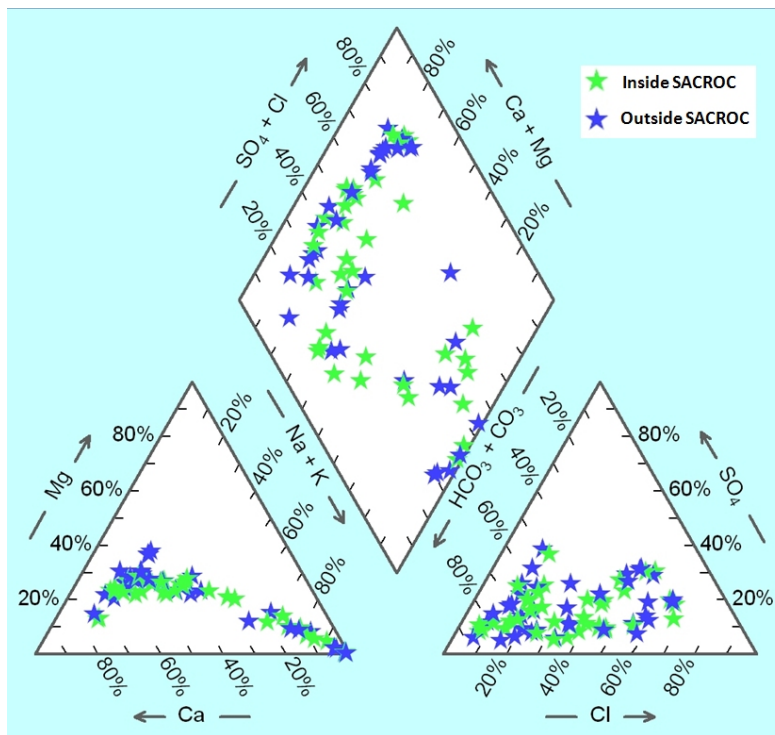


Figure 9. Piper diagram of BEG wells only showing no clear distinction between BEG groundwater samples collected inside SACROC versus outside SACROC.

A plot of sulfate (SO_4) versus chloride (Cl) anions (Figure 10) shows a more distinct grouping of samples from inside versus outside SACROC. BEG freshwater samples from inside have higher Cl values than those collected outside SACROC. Samples with higher Cl and SO_4 concentrations (e.g., Permian and produced water samples) have much higher total dissolved solids (TDS) than BEG freshwater samples. Trends of major element concentrations in figures 8 and 9 suggest mixing of Dockum aquifer groundwater and water with Permian and production-zone geochemical signatures. Mixing models tested using PHREEQC code at BEG predict that <1% produced oil field brine or 12% Permian water could mix with the lowest TDS BEG Dockum freshwater sample to produce the highest TDS Dockum sample.

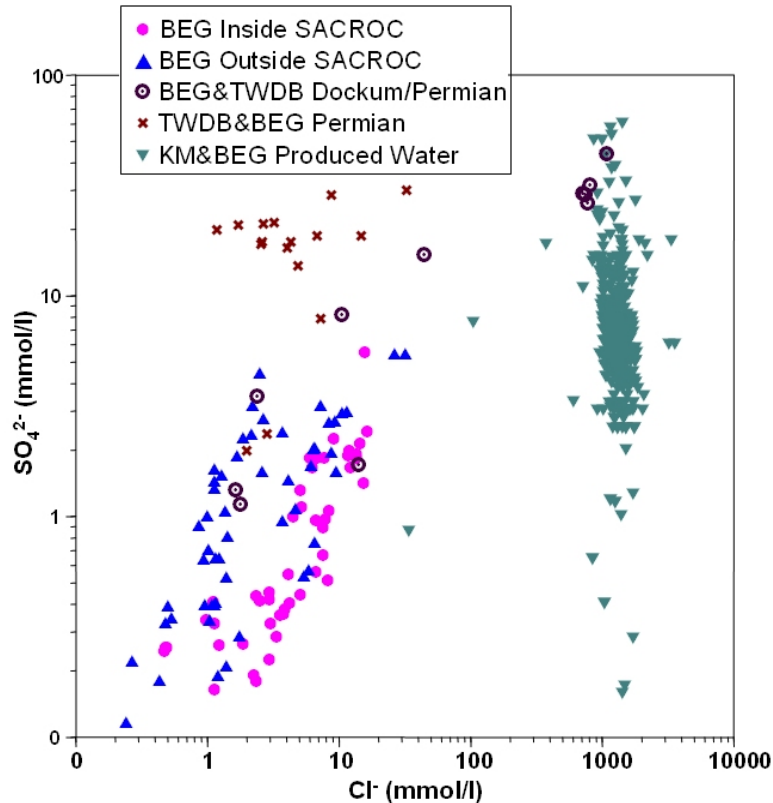


Figure 10. Sulfate vs. chloride concentrations of all BEG samples (five sampling periods, inside and outside of SACROC) and BEG and KM produced water samples.

Several mechanisms can be used to explain fluid mixing, especially in oil fields that have been operating since the early 1950s. Evidence of fluid mixing over SACROC should not be taken as proof of brine (or associated CO_2) leakage from compromised production and/or injection well casings. Historical oil-field practices did not take the environmental impacts of co-produced brine disposal into account. Use of unlined surface pits for disposal of co-produced oil-field brine was routine practice up until the mid-1960s and was not abandoned in Texas until the mid-1970s. In the US, many cases have been documented of oil-field brine contamination of groundwater resulting from brine discharge into streams or ponds, pipeline leaks, and infiltration pits (e.g., Reed, 1961; Fisher and Sublette, 2005; Kharaka et. al., 2005). Incidents of casing leaks have most likely occurred over the ~60-yr history of oil-field activity at SACROC. However, current KM operational practices, including use of protective surface casing and extensive

cathodic protection networks, make conduit flow between the ~7,000-ft-deep production and freshwater zones highly unlikely.

The main question pertinent to this study 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 aquifer water overlying SACROC, we would also expect to see impacts from high CO₂ concentrations. Given the complexity of the natural system and the likely signal from early oil-field activities, it is unrealistic to try to prove that no upward vertical communication of fluids has occurred in SACROC oil field. Evidence presented here allows us to say that no obvious impacts to groundwater are found, and that the impacts observed are not a result of interaction of freshwater with large volumes of injected CO₂.

More detailed description of the shallow subsurface stratigraphy underneath SACROC allowed us to construct a potentiometric surface map using water levels from only those wells completed in the Dockum Santa Rosa subunit of the Dockum aquifer. This map reveals a groundwater mound over SACROC (insert with cross section location lines in figure 11). One way to assess if shallow freshwater resources have been impacted by CO₂ injection at SACROC is to look at profiles of chemical constituents along Dockum aquifer groundwater flow paths in vicinity of SACROC (figures 11 through 13). There are no clear trends of lower pH, higher TDS, or higher concentrations of other analytes over SACROC versus areas downgradient from SACROC.

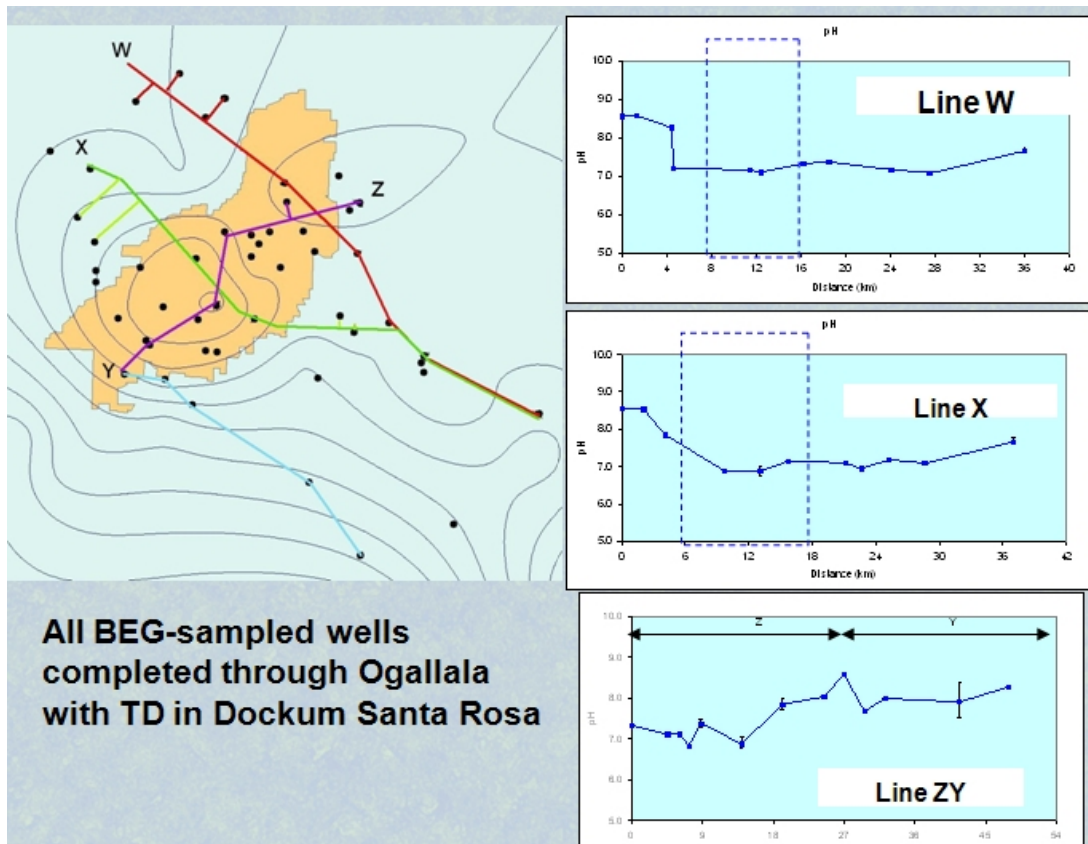


Figure 11. (a) Locations of transect plots relative to SACROC and potentiometric surface contours of Dockum Santa Rosa and (b) pH along gradient-parallel transects W, X, and ZY.

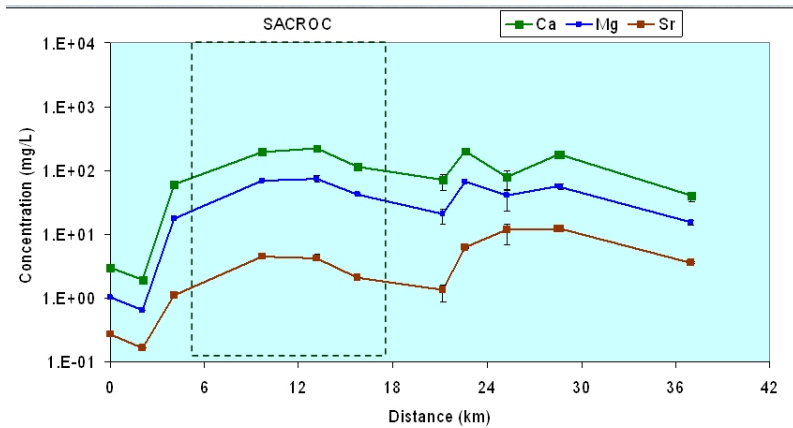


Figure 12. Calcium (Ca), Magnesium (Mg), and Strontium (Sr) concentrations along flow path transect line X.

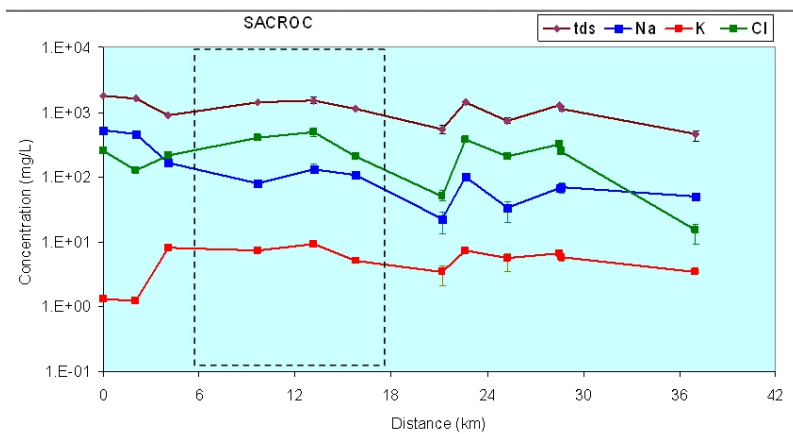


Figure 13. Total dissolved solids (tds), sodium (Na), Potassium (K), and Chloride (Cl) concentrations along flow path transect line X.

Another way to evaluate data from Dockum groundwater samples is to assess degradation of water quality by comparing analyte concentrations with EPA drinking water standards. Data summarized in Table 3 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 below 2. No preservative was added to anion samples. Some Dockum freshwater samples have constituents that exceed drinking water samples. The percentage of BEG Dockum aquifer samples taken from 60 wells and 1 spring with analytes exceeding EPA primary maximum contaminant levels (MCLs) and secondary drinking water standards are highlighted in yellow in Table 3. Without exception, the percentage of samples with analytes in excess of EPA standards is higher outside than inside SACROC (Table 3).

Arsenic (As) and lead (Pb) are listed as contaminants of particular concern in the July 2008 EPA proposed rule. The concern is that such constituents will be leached from rocks in the appropriate GS reservoir 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 3). 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 SACROC.

Table3. 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>				
Aluminum (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 groundwater, produced water, injectate CO₂, solid carbonate phase, and plant matter, which forms the substrate for microbial oxidation of CO₂. Potential contributions to the carbon isotope signature include mixing with Permian and produced water, microbially produced CO₂, and injectate CO₂. A plot of carbon isotope ratios versus dissolved inorganic carbon (DIC) shows an increase in light carbon with increasing DIC. This datum is consistent with input from microbial CO₂ but does not rule out the presence of injectate CO₂. Modeling of the system is underway to test if it is sensitive to injected CO₂ and if so, if any injected CO₂ can be identified.

BEG researchers are currently collecting water levels in Dockum aquifer wells throughout Scurry County. Our objective is to generate potentiometric surface maps for the various stratigraphic intervals that compose the Dockum aquifer. These maps will aid in reactive transport modeling and further interpretation of Dockum aquifer groundwater chemistry.

Geochemical modeling results

Sediment reactivity in the Dockum

Dockum aquifer sediments are predominantly siliciclastic with small amounts (1%) of diagenetic and detrital calcite. Visual inspection of Dockum well cuttings collected from SACROC indicate a general composition of 60-80% quartz, 10-20% feldspar, 15% dark rock fragments and minor carbonate cements. SEM aided by an Energy Dispersive X-ray system shows mineralogical content of the following: quartz > K-feldspar > albite > dolomite > calcite. Quartz grains show no evidence of overgrowth or corrosion; however, feldspars show limited dissolution features. Clay, mostly smectite, coats most mineral grains. Dolomite (5 %) occurs as ubiquitous rhombic crystals that often exhibit corrosion suggesting dissolution.

The degree of influence of carbonate minerals in the predominantly siliciclastic Dockum aquifer was assessed using co-variation of SiO₂ and HCO₃⁻ after Hounslow (1995). Data collected inside and outside SACROC, and from the TWDB database (Fig. 14) show that in spite of the volumetric dominance of silicates in the Dockum, samples are geochemically dominated

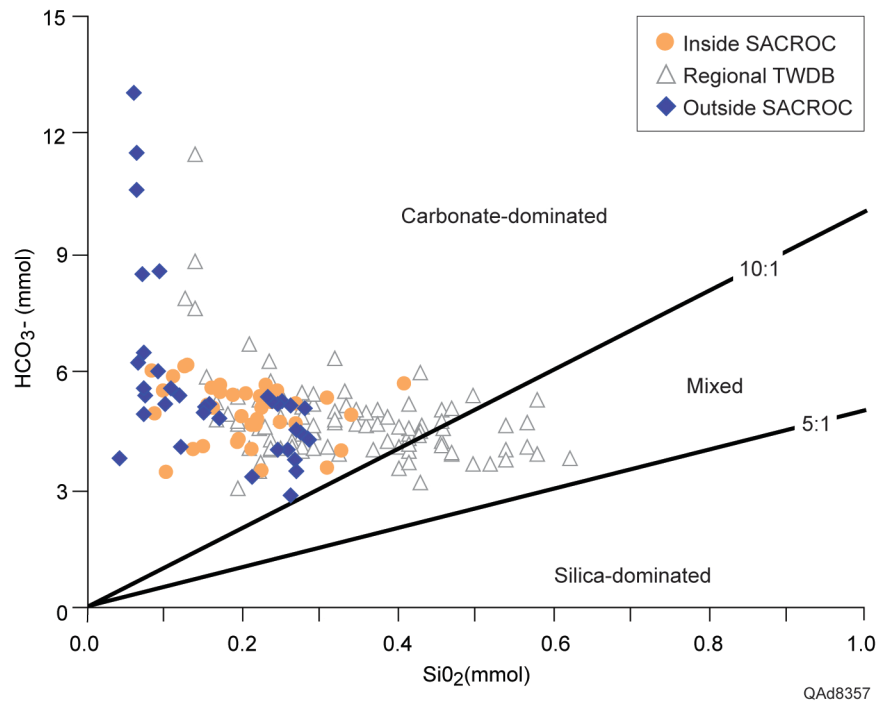


Figure 14. Plot showing the relative influences of carbonate and silicate geochemistry in the Dockum aquifer near SACROC.

by carbonate weathering. Regional data also indicate the same importance of carbonate geochemistry with a relatively minor influence of silicate weathering, most likely representing feldspar dissolution. Overall, these geochemical co-variations suggest that small amounts of carbonate in an aquifer (1 to 5 % in this case) may yield a geochemistry receptive to changes in CO_2 , supporting the hypothesis that carbonate parameters may be useful indicators of leakage. This conclusion is in direct opposition to the assumption of Wilkin and Digiulio (2010) who argue that a quartz-rich aquifer would be non-reactive.

Major element trends

A classic piper diagram (Piper, 1944) displaying normalized values for cations (lower left triangle), anions (lower right triangle) and a combination of the two (central diamond) was used to graphically indicate water type, mineral reactions, mixing, and ion exchange (Fig. 15). Dockum samples plot in all quadrants of the piper diagram, indicating a geochemical environment with many influences but little distinction between samples collected inside and outside SACROC. As expected, Permian waters which reside in evaporite-containing formations plot in the gypsum field indicating CaSO_4 -type waters. Waters co-produced with oil are predominantly NaCl-type. General trends on the anions triangle indicate two types of mixing: the majority of samples outside SACROC appear to trend towards Permian compositions, while a majority of samples inside SACROC (and a few outside SACROC) appear to trend towards produced water compositions. The suggestion is that variable amounts of mixing of Dockum water with Permian and co-produced brines affect the geochemistry of the Dockum at SACROC.

A trend stretching from Na^+ to Ca^{2+} on the cation triangle further suggests that input of NaCl brines into the Dockum results in the exchange of Na^+ for Ca^{2+} on exchange sites. In the case of SACROC, the exchange of Na^+ in solution for Ca^{2+} sorbed to clays is fueled by mixing of Dockum and produced waters. Therefore two mechanisms exist by which calcium ions are added

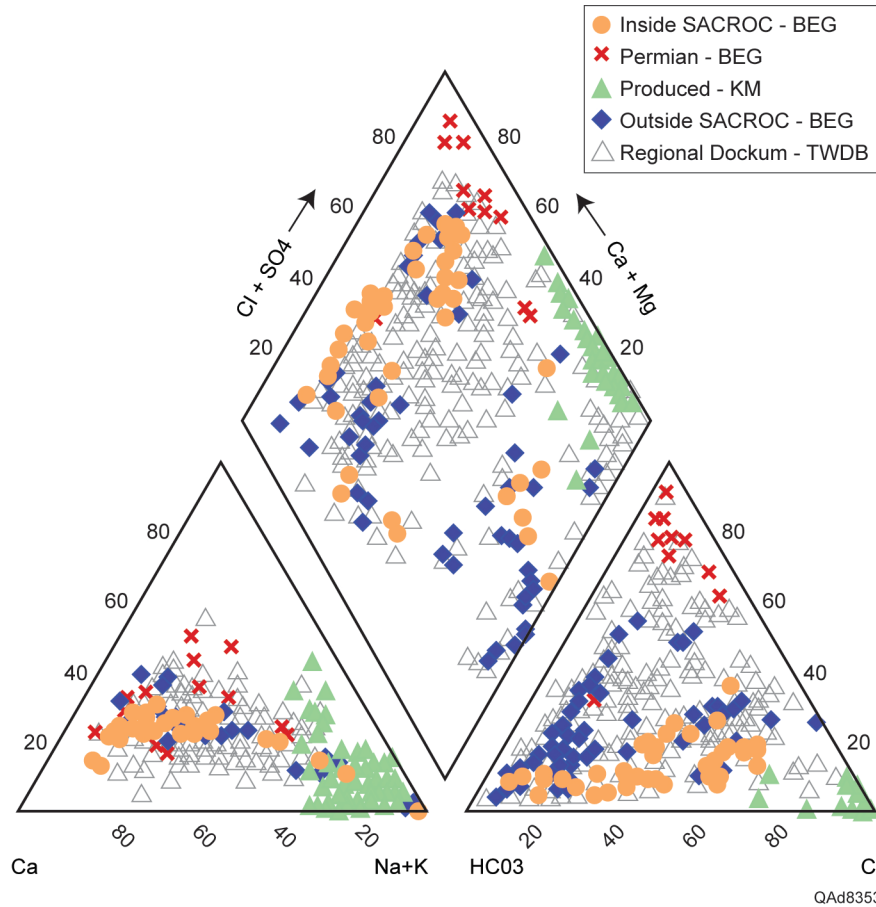


Figure 15. Piper diagram showing compositions of samples from Dockum and Permian formations collected by the BEG during the study. Also shown are analyses provided by Kinder Morgan for produced brines and historical Dockum analyses furnished by the TWDB.

to the shallow groundwater system: one a natural process inherent to the regional system (mixing with CaSO_4 -type waters in the salt dissolution zone), and the other resulting from land-use practices (mixing with co-produced brines and cation exchange). Evidence that both processes are at work can be seen in relatively weak co-variations between Ca^{2+} and SO_4^{2-} that strengthen significantly when addition of a NaCl component and cation exchange is also considered (Fig. 16). A general decrease in Cl^- with depth (not shown) indicates that NaCl input is likely from historical disposal of brine into surface pits rather than from brine migrating from the deep production reservoir.

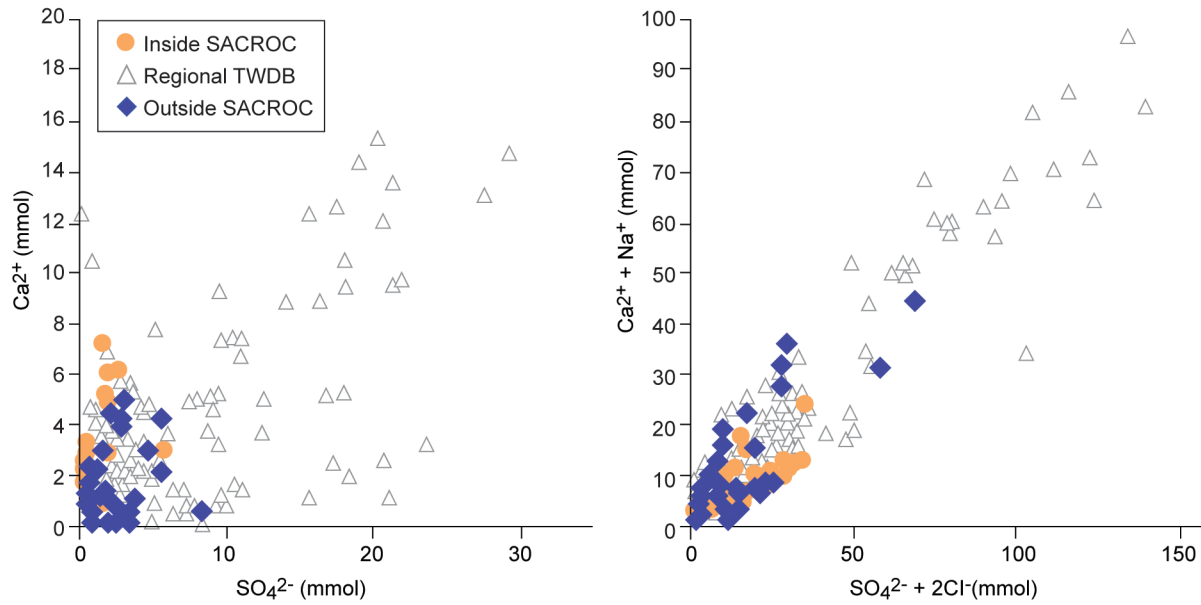
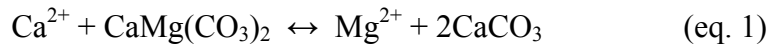


Figure 16. Co-variation of Ca^{2+} with SO_4^{2-} (left) is not particularly strong, indicating Ca^{2+} is not solely supplied to the system by mixing with Permian CaSO_4 waters. Addition of an NaCl produced water component with cation exchange (right) shows even stronger correlation indicating both processes contribute to the input of calcium ions to the shallow aquifer.

Dedolomitization

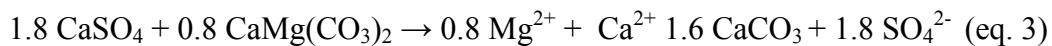
As described by Appelo and Postma (2007), the mass balance for the dedolomitization reaction driven by input of calcium ions is defined as follows:



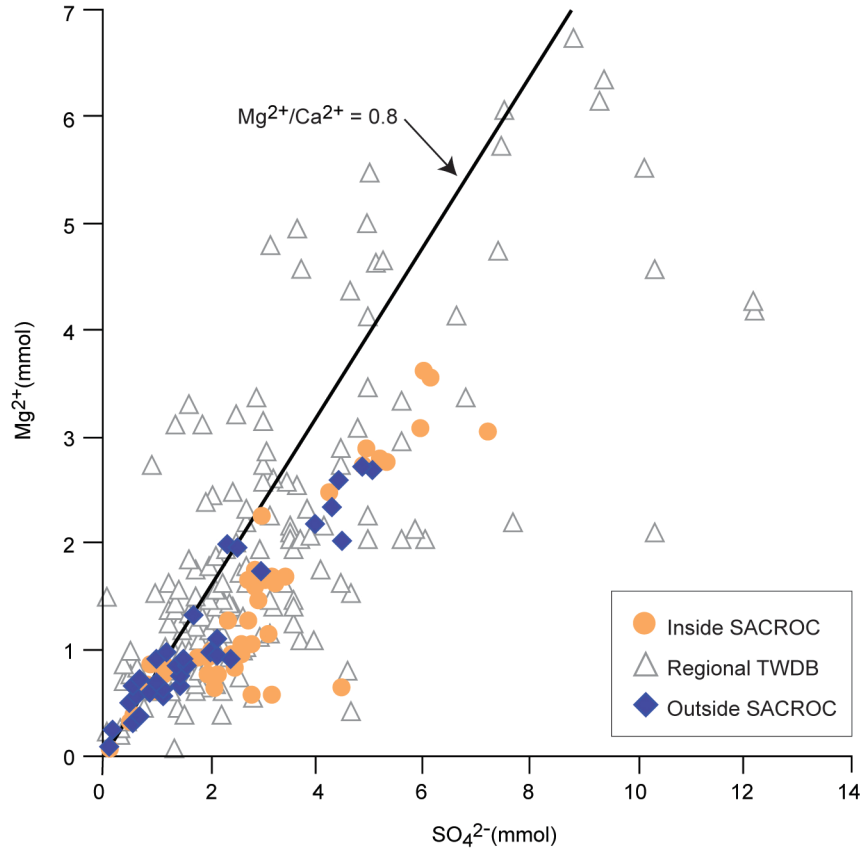
where two moles of dolomite dissolve for every mole of calcite that precipitates. The equilibrium condition for this reaction at 25°C is defined as:

$$K = \text{Mg}^{2+}/\text{Ca}^{2+} = K_{\text{dol}}/(K_{\text{cal}})^2 = 10^{-17.09}/(10^{-8.48})^2 = 0.8 \quad (\text{eq. 2})$$

The equilibrium condition is represented by $\text{Mg}^{2+}/\text{Ca}^{2+} = 0.8$, irrespective of the absolute values of these two ions in the system. Ratios of $\text{Mg}^{2+}/\text{Ca}^{2+} < 0.8$ therefore represent a system that favors dolomite dissolution and calcite precipitation (dedolomitization). The mass transfer necessary to conserve the equilibrium condition of $\text{Mg}^{2+}/\text{Ca}^{2+} = 0.8$ is as follows:



which further indicates that Mg^{2+} , Ca^{2+} , and SO_4^{2-} should all increase during dedolomitization. Strong co-variation between Mg^{2+} (an indicator of dolomite dissolution) and SO_4^{2-} (an indicator of Ca^{2+} input) with $\text{Mg}^{2+}/\text{Ca}^{2+} < 0.8$ should be expected and Fig. 17 illustrates these relationships in the Dockum aquifer near SACROC.

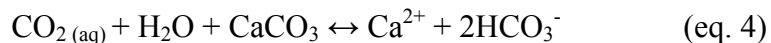


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Figure 17. Co-variation of Mg^{2+} and Ca^{2+} indicates a chemical driving force for dedolomitization.

Modeling the role of CO_2 in a system undergoing dedolomitization.

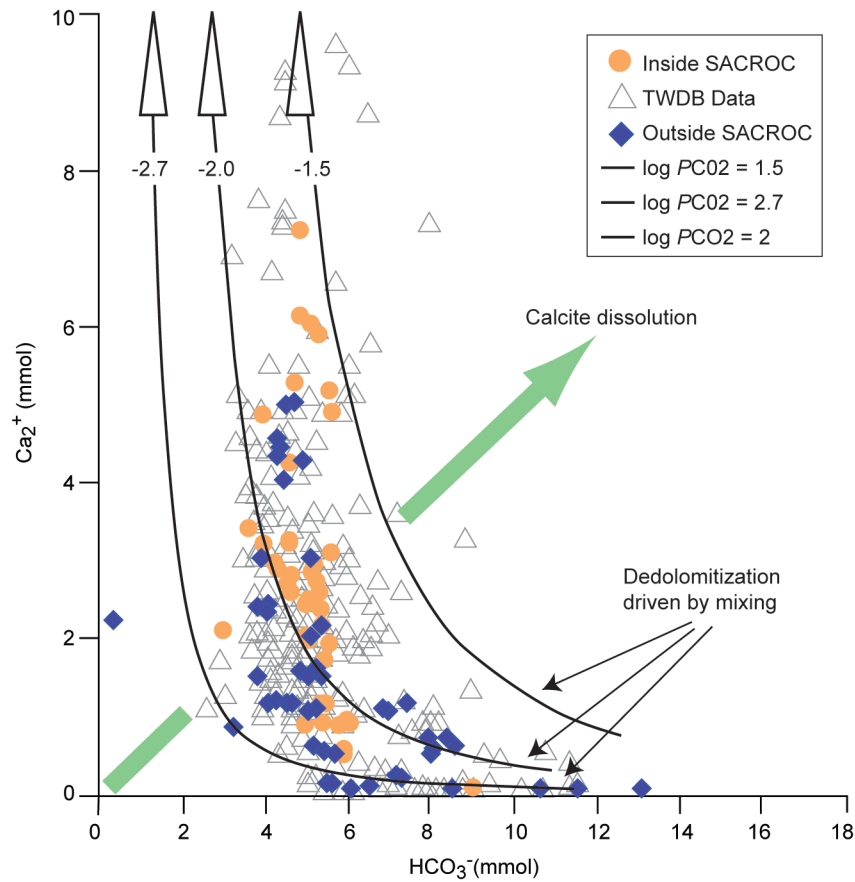
The conclusion that Ca^{2+} rather than CO_2 , is driving the carbonate system is significant because it illustrates that changes in carbonate equilibrium are not necessarily indicators for CO_2 input but can be fueled by mixing. Dedolomitization creates a significantly different carbonate environment than that of simple calcite dissolution. Whereby calcite dissolution is driven by CO_2 according to the reaction:



dedolomitization is driven by calcium ions, which combine with carbonate supplied by dolomite dissolution to form calcite (eq.1). The driving forces (products) and the outcomes (reactants) of these two environments are very different illustrating the importance of defining the system before predicting the effects of CO_2 .

With the overall system well-defined, the PHREEQC code (Parkhurst and Appelo, 1999) was used to constrain the role of CO_2 in a system dominated by dedolomitization rather than calcite dissolution. During calcite dissolution fueled by CO_2 (eq. 4), 1 mole of Ca^{2+} and 2 moles of HCO_3^- are produced and data will trend along a line with a slope of 0.5 on a plot of Ca^{2+} versus HCO_3^- (shaded arrow in Fig. 18). As expected, data do not follow calcite dissolution trends but rather fall within a range of trends modeled for dedolomitization under several conditions of constant PCO_2 . These trends were constructed by mixing 25 mmoles of $CaSO_4$ to

Dockum water initially in equilibrium with calcite and dolomite at various fixed PCO_2 . Data correspond with these trends and generally lie within the boundaries defined by the range of constant PCO_2 from $10^{-2.7}$ to $10^{-1.5}$ (Fig. 18).



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Figure 18. Modeling results for evolution of Ca^{2+} and HCO_3^- during calcite dissolution and dedolomitization. Modeled curves for dedolomitization under constant PCO_2 are shown for $10^{-1.5}$, $10^{-2.0}$, and $10^{-2.7}$.

During dedolomitization under constant PCO_2 , geochemical evolution progresses from high to low HCO_3^- and from low to high Ca^{2+} . This is in contrast to the trend for calcite dissolution which is from low to high HCO_3^- and Ca^{2+} . Numerical modeling shows that dissolved bicarbonate in the initial solution slows dolomite dissolution in the early stages of reaction by supplying some anions necessary for calcite precipitation. As calcite precipitates, dissolved bicarbonate and calcium are quickly used, resulting in decreasing HCO_3^- and relatively steady concentrations. As the dissolved bicarbonate in the initial water is consumed, dolomite dissolves and calcite precipitates and the kinetics of dissolution/precipitation reactions control ion concentrations in the water. If the system re-equilibrates to a higher constant PCO_2 under the normal aquifer conditions observed at the study site (PCO_2 from $10^{-2.7}$ to $10^{-1.5}$), the mass of dolomite dissolution increases, the mass of calcite precipitation decreases, HCO_3^- increases and pH decreases, all at higher constant PCO_2 . Without knowledge of the system, it might appear that the high bicarbonate samples, those with HCO_3^- higher than about 10 mmoles, are anomalously impacted by CO_2 . However, with the knowledge that the system is undergoing

dedolomitization in response to complex mixing and cation exchange relationships, it is apparent that these samples are in fact the least “evolved” or reacted samples in the system.

Sensitivity of the system to CO₂ input

With the geochemical system defined, it is possible to predict the sensitivity of the system to CO₂ input and to identify the geochemical parameters that will best signal this input. When the data in Fig. 18 are visually compared to the modeled trends for constant *PCO₂* it becomes apparent to the eye that the data trend toward higher *PCO₂* with evolution. For example, the majority of samples with relatively low Ca²⁺ of about 2 mmoles cluster near an average modeled *PCO₂* trend of about 10⁻²; however, when these samples have evolved to higher Ca²⁺ concentrations of about 7 mmoles, they cluster near higher modeled *PCO₂* of 10^{-1.5} suggesting that CO₂ is building in the system.

The observed phenomenon of increasing *PCO₂* could result from CO₂-EOR practices; however, no geochemical distinction has been observed between samples collected inside and outside SACROC that would suggest impact from CO₂ injection. In addition, the modern data collected during the study both inside and outside SACROC show no geochemical distinction from TWDB historical regional data collected from areas spatially and/or temporally removed from CO₂ injection. Groundwater quality inside SACROC is not significantly degraded compared to EPA drinking water standards (Smyth et al., 2009). Redox reactions producing HCO₃⁻, especially sulfate reduction, may play a role; however, aquifer conditions were generally found to be highly oxidizing. We conclude that, based on PHREEQC model output, increases in *PCO₂* represent normal system degassing during dedolomitization. Current analysis of carbon isotope data is underway to confirm this conclusion.

To simulate the perturbations that would occur if the potable aquifer were to receive CO₂ from the storage reservoir due to a leak, a sensitivity analysis was performed using the system model and the PHREEQC code. In the case of leakage into an aquifer experiencing dedolomitization, two mass transfers into the aquifer occur simultaneously and affect the intricate interplay between HCO₃⁻ and Ca²⁺: 1) mass transfer of Ca²⁺ from mixing and/or cation exchange and, 2) mass transfer of CO₂ from a simulated leak. Ca²⁺ input is essentially a function of the hydrodynamic factors producing mixing and can be assumed to be a steady-state process for each environment that is modeled. With a constant rate of mixing and mass flux of Ca²⁺ into the system, a leakage signal can be modeled as an increase in CO₂ input which, when compared to a defined steady influx of Ca²⁺, manifests as an increase in CO₂/Ca²⁺. Alternately, this ratio can also be varied and used to represent different conditions of mixing that exist in different aquifers having different hydrodynamics. Because CO₂/Ca²⁺ is independent of absolute fluxes, the ratio can be used to represent a variety of different environmental fluxes and conditions.

To understand how systems react to CO₂ and to discern the geochemical parameters most useful for monitoring GS sites, two types of analyses are useful: one that addresses how carbonate parameters will respond to different inputs of CO₂ within a given system and one that addresses the range of geochemical responses that would arise from the geologic variability among sites. Both analyses use the response of carbonate parameters such as calcite and dolomite dissolution, DIC, HCO₃⁻, pH, and Ca²⁺ to variations in CO₂.

The first analysis determines the sensitivity of a defined system, in this case, the Dockum aquifer above SACROC, to different magnitudes of CO₂ input. This approach achieves two important goals: 1) to illustrate the magnitude of CO₂ input that would be necessary to discern leakage signal from background noise, and 2) to evaluate the sensitivity of individual carbonate

parameters to CO₂ within that system. If a system is insensitive to CO₂ input, geochemical parameters will not sufficiently signal a leak in its beginning stages. If a system is sensitive, geochemical parameters may be useful for monitoring because they would signal a leak in its early stages, providing greater options for protecting resources and/or remediation.

The second type of analysis considers the degree to which site-specific factors can affect how carbonate parameters behave in the presence of CO₂. Such an analysis considers the importance of understanding the specific hydrochemical characteristics of each aquifer that exists over a GS site, evaluates the importance of detailed characterization of each aquifer system, and determines the degree to which assumptions can be made based on small data sets. For example, if the magnitude and direction of change of geochemical parameters is similar in any environment, these parameters will be useful for monitoring GS sites. If, however, site specific conditions create wide-ranging affects and outcomes, their usefulness is decreased because intricate and costly characterizations at each site would be necessary.

Quantifying the modeled geochemical changes for the first approach described above is accomplished by calculating the percent difference between the beginning and resulting geochemical parameters after adding CO₂ into a system based on the following equation:

$$\% \text{ Change} = \left| \frac{x1 - x2}{x1} \right| \times 100 \quad (\text{eq. 5})$$

Where $x1$ is the beginning composition of the parameter being analyzed and $x2$ is the composition of that parameter after CO₂ input. This type of analysis will identify the response of the system and form the basis for comparing the sensitivity of individual geochemical parameters.

A similar approach is used to estimate how various aquifers with site-specific geochemical characteristics will react to CO₂ input. This analysis gives information on the error that would result, for example, if the simple model of calcite dissolution is assumed in an aquifer that is actually experiencing dedolomitization. In this case, it is appropriate to use the equation for percent error:

$$\% \text{ Error} = \frac{\text{Assumed} - \text{Actual}}{\text{Actual}} \times 100 \quad (\text{eq. 6})$$

Where *Assumed* is the value calculated under the assumption of calcite dissolution and *Actual* is the value that would be expected from our model under dedolomitization. Unlike the percent difference calculation in eq. 5, this result will give a directional analysis, indicating if the error would underestimate or overestimate the actual value.

The initial sensitivity simulation is structured to define the amount of CO₂ needed to create the observed CO₂ increase shown by the data in figure 18. A starting water composition is chosen at the point in the system where PCO_2 appears to shift to higher values (about 4.5 mmoles HCO₃⁻ and 1 mmole Ca²⁺). The ending composition is chosen to represent the magnitude of the shift that is visually observed in the dataset (about 5 mmoles HCO₃⁻ and 9 mmole Ca²⁺). CO₂/Ca²⁺ = 0.1 yields results that represent the spread of regional TWDB data. The model results indicate that the shift toward higher PCO_2 in the data is consistent with the addition of 1.5 mmoles of CO₂ and 15 mmoles CaSO₄ at a CO₂/Ca²⁺ ratio of 0.1.

To continue the analyses using the same initial water composition, we then added CO₂ to the system using CO₂/Ca²⁺ ratios of 0.1, 0.5, 1, 2, and 10 to understand how different conditions of mixing would manifest similar CO₂ inputs. The evolutionary trends for the varying CO₂/Ca²⁺ ratios are shown in Fig. 7 (broken lines) along with calcite dissolution (solid line). Results show trends different from the evolution of waters modeled under constant PCO_2 (Fig. 18). In systems

with less input from mixing (i.e. with greater $\text{CO}_2/\text{Ca}^{2+}$), reaction pathways shift to higher HCO_3^- and lower Ca^{2+} and more closely mimic calcite dissolution, although dolomite continues to dissolve and calcite continues to precipitate.

Points of equal CO_2 input are shown by solid triangles in Fig. 7 for 1.5 mmoles and 6 mmoles for each environment defined by a specific relative rate of mass transfer ($\text{CO}_2/\text{Ca}^{2+}$) and for straight calcite dissolution. Model output for addition of 1.5, 6 and 50 mmoles CO_2 . Background geochemical variability at SACROC is represented by the spread of regional data collected in areas devoid of CO_2 injection and those collected outside SACROC as indicated by a shaded area in Fig. 19. Sensitivity analysis shows that 6 mmoles of CO_2 is necessary to achieve Ca^{2+} and HCO_3^- compositions outside of background concentrations. Also evident from the simulations is that a system undergoing calcite dissolution is slightly less sensitive to CO_2 input than one undergoing dedolomitization.

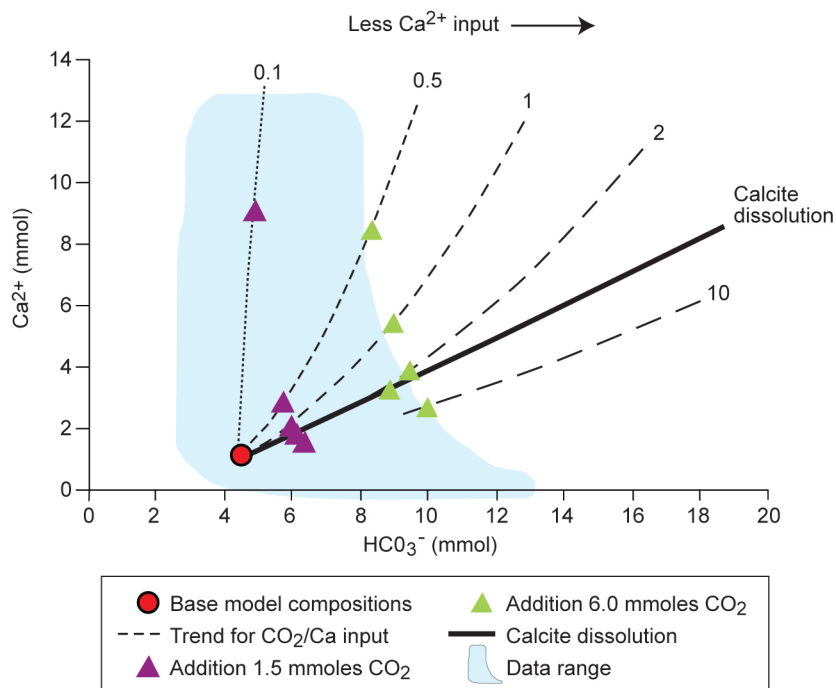
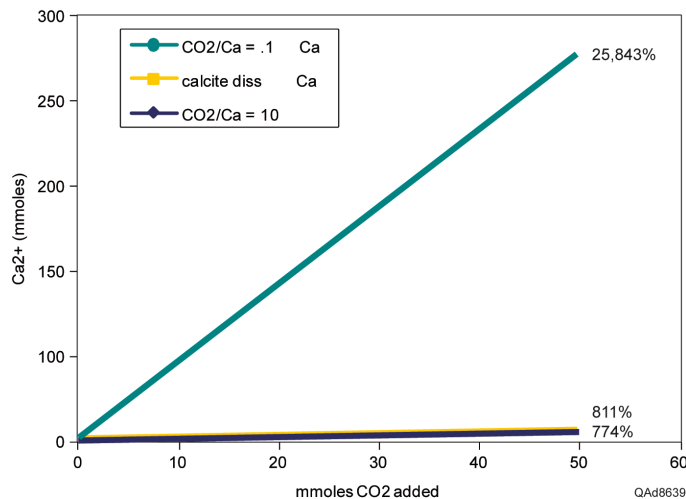
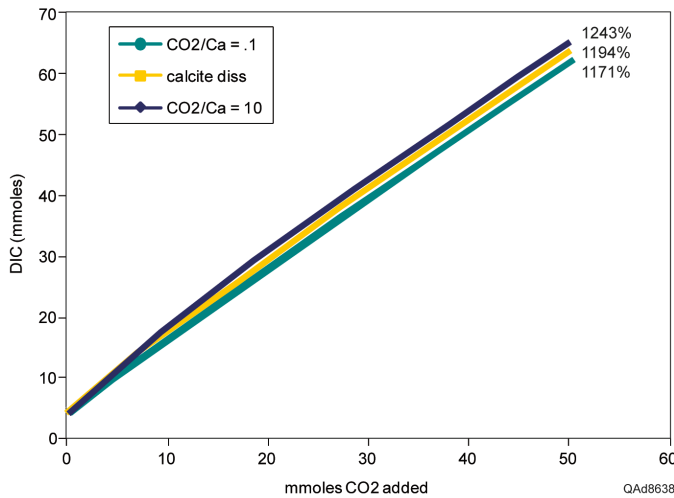


Figure 19. Results of CO_2 sensitivity modeling. Shaded area represents background geochemical variation in the aquifer. Beginning composition for all models is denoted by a red dot. Ending compositions are shown by triangles. Responses of the system to various mass inputs of CO_2 under different mixing conditions are shown.

To understand the significance of 6 mmoles of CO_2 input into an aquifer with regard to leakage rate from a storage formation, a mass balance exercise was performed using the anthropogenic emissions expected from a 500 Megawatt (MW) power plant, which is assumed to produce and store up to 3 million tonnes/year of carbon dioxide (MIT Interdisciplinary Study, 2010). Assumptions are: 1) a saturated aquifer thickness of 60 m with a porosity of 0.30, 2) an area of consideration within the aquifer of 1 hectare; and 3) any CO_2 leaked from the storage reservoir is instantaneously and equally distributed throughout the area of consideration. We have discerned, through careful inspection and modeling of the hydrochemical environment at SACROC, that the CO_2 concentration necessary to produce a geochemical signature above

background conditions is 6 mmol/L. This equates to 4.75×10^6 g of CO_2 within the 1 hectare area and represents 0.001% leakage rate of the total yearly output from a 500 MW power plant. The system appears sensitive enough to detect a relatively small leak. However, because the model assumes instantaneous distribution throughout the area of consideration, this is a conservative estimate that depends on the type and areal distribution of the leak. If the leak enters the aquifer as a point source, the geochemical signal will be strong but difficult to locate spatially. If the leak enters the aquifer more diffusely, the geochemical signal will be weaker but easier to locate spatially. The calculation described herein is more applicable to the latter case.

To identify which carbonate parameter is best-suited for monitoring at a variety of sites, it is necessary to understand how each parameter responds during carbonate dissolution and under different conditions of leakage versus mixing during dedolomitization. The most desirable parameter will have the highest sensitivity to increasing CO_2 input (i.e. the largest variability) and the magnitude and direction of its variability should be similar, and therefore predictable, in any environment. The modeled responses of DIC, HCO_3^- , pH, and Ca^{2+} to increasing CO_2 input are presented in Fig. 20 for $\text{CO}_2/\text{Ca}^{2+} = 0.1$ and 10 and for calcite dissolution, representing the range of expected environmental responses.



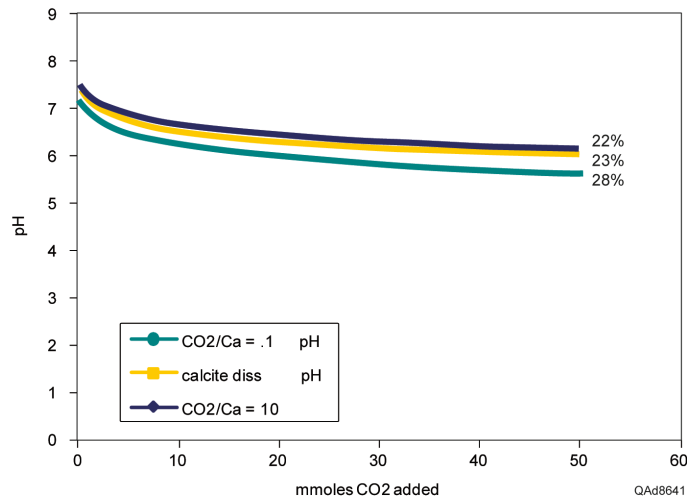
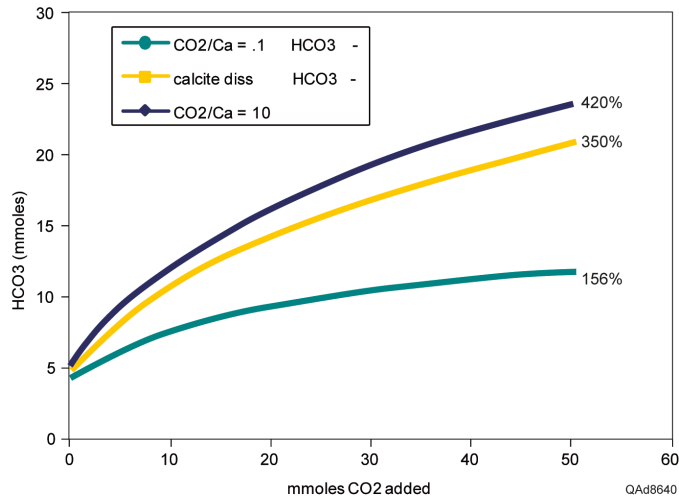


Figure 20. Percent change from starting composition for various carbonate parameters during modeled input of CO₂ (x axis). Parameter responses for a range of environments undergoing dedolomitization and calcite dissolution are shown with values for percent change noted beside respective trends. DIC shows the highest and most predictable variability.

Of the four parameters, DIC has the highest sensitivity with the largest and most consistent changes from the starting composition (1171%, 1194%, and 1243% for CO₂/Ca²⁺ = 0.1, calcite dissolution, and CO₂/Ca²⁺ = 10, respectively). Although Ca²⁺ also shows relatively high sensitivity, its variability is large (ranging from 774% to 25,843%) and unpredictable and depends heavily on the flux of Ca²⁺ into the system via mixing. Predicting this outcome necessitates knowledge of mixing relationships which require in-depth characterization of hydrodynamics, therefore disqualifying Ca²⁺ as a useful global monitoring parameter. HCO₃⁻ exhibits the next greatest sensitivity (ranging from 156% to 420% change from initial composition) but with a highly variable magnitude. This is due to the pH-dependence of the distribution of carbonate species (H₂CO₃, HCO₃⁻, CO₃²⁻) in natural waters which complicates interpretation of HCO₃⁻ concentrations with regard to mass of CO₂ that has entered the aquifer. A relatively consistent magnitude and range of variation is shown by the response of pH to CO₂ input (28%, 23%, and 22% for CO₂/Ca²⁺ = 0.1, calcite dissolution, and CO₂/Ca²⁺ = 10,

respectively), but sensitivity is relatively small and may be difficult to recognize apart from natural variability.

Similarly, the percent errors that would be incurred using each parameter to assess a system undergoing dedolomitization under the assumption of calcite dissolution are presented in Table 4 for 6 and 50 mmoles CO₂ input at varying values of CO₂/Ca²⁺. Errors for calcium concentrations are large (from 971% to 33,813%) and again disqualify this parameter as useful for monitoring. Of the remaining parameters (DIC, HCO₃⁻, and pH), errors are bidirectional with some dedolomitization environments yielding parameter concentrations lower and some higher than expected from calcite dissolution. HCO₃⁻ shows the largest ranges in error (39.03% for 6 mmoles CO₂ input and 58.17% for 50 mmoles CO₂ input). DIC (11.11% and 5.37% for 6 and 50 mmoles CO₂ input, respectively) and pH (6.08% and 8.47% for 6 and 50 mmoles CO₂ input, respectively) exhibit smaller ranges in error. The results indicate that changes due to CO₂ input in an uncharacterized system would be difficult to predict and even more difficult to quantify reliably illustrating the necessity of understanding the system before correct leakage assessment can occur.

Table 4. Percent error that would result if a system undergoing dedolomitization is assessed assuming calcite dissolution. Mean, range, and standard deviation are shown.

6 mmoles CO ₂ added						
CO ₂ /Ca ²⁺	CO ₂ added (mmoles)	Ca ²⁺ added (mmoles)	DIC (%)	HCO ₃ ⁻ (%)	pH (%)	Ca ²⁺ (%)
0.1	6	60	-2.38	-26.47	-5.19	4160.87
0.5	6	12	2.38	-5.88	-1.93	971.01
1	6	6	4.76	1.47	-0.74	582.61
2	6	3	6.35	6.79	0.00	392.75
10	6	0.6	8.73	12.56	0.89	246.38
Mean	-	-	3.97	-2.31	-1.39	1270.72
Range	-	-	11.11	39.03	6.08	4407.25
Std. Dev.	-	-	4.24	15.12	2.36	1638.32

50 mmoles CO ₂ added						
CO ₂ /Ca ²⁺	CO ₂ added (mmoles)	Ca ²⁺ added (mmoles)	DIC (%)	HCO ₃ ⁻ (%)	pH (%)	Ca ²⁺ (%)
0.1	50	60	-2.52	-43.27	-7.48	33,813.04
0.5	50	12	-1.10	-18.75	-2.99	7276.81
1	50	6	0.00	-8.17	-1.66	3972.46
2	50	3	1.10	1.44	-0.50	2334.78
10	50	0.6	2.99	14.90	1.00	1059.42
Mean	-	-	0.09	-10.77	-2.33	9691.30
Range	-	-	5.37	58.17	8.47	34,872.46
Std. Dev.	-	-	2.10	21.99	3.23	13,684.12

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Conclusions

Our field-based study of shallow (<500 ft) groundwater overlying and within an ~1,000 mi² area of SACROC shows no impacts to drinking water quality as a result of over 35 years of deep subsurface (6,000-7,000 ft) CO₂ injection. Modeling of stable carbon isotopes ($\delta^{13}\text{C}$) of injectate CO₂ gas, DIC in shallow and deep groundwater, carbonate mineral matrix, and soil zone CO₂ suggests that no significant injectate CO₂ has been introduced to the shallow groundwater.

Interpretation of groundwater flow regime, and concentrations of major ions and trace metals, indicate mixing of water types and water-rock interaction (i.e. dedolomitization) as major controls on groundwater geochemistry at SACROC. We think the popular assumption that carbonate parameters alone can be used as indicators of groundwater quality over a GS site is too simple, especially in complex hydrogeologic settings. We emphasize the importance of defining the regional groundwater system to (1) understand how it might react to introduction of CO₂ and (2) identify the parameters best suited for monitoring over GS sites. Research is ongoing to define and group major geochemical aquifer systems and to assess the protocol that would be appropriate for each group.

Aquifer sampling and analysis of site-specific conditions may be needed to understand how an aquifer system will react to CO₂ and the parameters best-suited for monitoring at sequestration sites. Research is ongoing to define and group major geochemical aquifer systems and to assess the protocol that would be appropriate for each group.

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