

# Executive summary: Recent results of the SACROC groundwater geochemistry summary

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## **Executive Summary: Recent results of the SACROC Groundwater Geochemistry Study**

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### **Executive Summary**

The purpose of this document is to report a summary of recent results and research of the SACROC groundwater quality study and their relation to geologic sequestration (GS) of CO<sub>2</sub>. The research was conducted by scientists at the Gulf Coast Carbon Center (GCCC) as part of the NETL Southwest Carbon Partnership Phase II (SWP) research. The results of this study were not available before the publication of the July 25, 2008, proposed rule, "Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (CO<sub>2</sub>) Geologic Sequestration (GS) Wells" (73 FR 43492). The work is currently being written for peer review publication in *Applied Geochemistry* to be submitted by the end of 2009, and is useful for consideration of amendments to the Safe Water Drinking Act. Additional details can be found in Smyth et. al., 2009; Romanak et. al., 2008 and 2009; and in the document, *Modeling shallow groundwater geochemistry and carbon isotopes: test of methodology for CO<sub>2</sub> storage evaluation at an EOR site, west Texas, USA*, published at <http://www.beg.utexas.edu/gccc/>.

Our examination of groundwater geochemistry at a site where CO<sub>2</sub> has been injected for decades shows that monitoring of natural parameters (pH, alkalinity, etc.) in shallow aquifers may be impractical and/or ineffective for evaluation of CO<sub>2</sub> storage permanence. At the very least, detailed analysis of background variability and processes controlling groundwater geochemistry would be required on a case by case basis to confirm correct interpretations. Our analysis shows that to detect possible CO<sub>2</sub> leakage into an underground source of drinking water (USDW) it is important to characterize the hydrogeologic context. Sampling at a few wells without understanding the hydrogeologic context could lead to erroneous interpretations. Errors could be either at sites where CO<sub>2</sub> leakage has occurred but is not detectable or at sites where non-injection induced changes are mistakenly assumed to indicate leakage. We have found that background variability in aquifers may mask the effects of even moderate anthropogenic CO<sub>2</sub> input at GS sites rendering it impossible to discriminate changes in natural biogenic CO<sub>2</sub> from anthropogenic inputs.

### **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<sub>2</sub> is adequately sequestered with respect to the biosphere. Research regarding the impact of CO<sub>2</sub> leaks on potable aquifers is focused on, 1) assessing geochemical outcomes of increased CO<sub>2</sub> and their effects on drinking water quality, 2) determining the potential for widespread usage of shallow aquifer geochemistry for CO<sub>2</sub> storage evaluation and, 3) identifying the parameters best suited for monitoring groundwater resources.

The success of using shallow groundwater geochemistry as a tool for CO<sub>2</sub> 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 CO<sub>2</sub> to the aquifer. This requires a shift that is larger than normal background variability and is therefore detectable as an indicator of change. Widespread application of these methods in a variety of GS locations also necessitates that the type and magnitude of geochemical shift is similar or at least predictable in any geochemical environment even though processes and mineralogies differ widely among aquifers.

Indeed the position of many researchers is that a predictable consequence of input of CO<sub>2</sub> into a dilute aquifer is an increase in dissolved inorganic carbon (DIC) as alkalinity, H<sub>2</sub>CO<sub>3</sub> or HCO<sub>3</sub><sup>-</sup>, a decrease in pH, and mobilization of cations including toxic metals from mineral dissolution and desorption reactions (Assayag et. al., 2009; Apps, et. al., 2009; Carroll et. al., 2009; Wang and Jaffe, 2004). A popular suggestion is that these parameters are therefore suitable for monitoring groundwater resources. The results of the SACROC ground water study, which is the only field study to date of potable water at a large-scale industrial CO<sub>2</sub> storage analogue, give strong evidence against such assumptions. At SACROC, natural and man-induced processes that are common in many shallow aquifers have created; 1) a geochemical system that is more complex and reacts differently to CO<sub>2</sub> than the simple system put forth by previous researchers, and 2) a background variability that would mask even a relatively large-scale exogenous CO<sub>2</sub> input. The implications are that GS monitoring strategies using natural groundwater constituents must, at the very least, be site-specific and may not be useful at all owing to the variability and complexity of groundwater systems.

### **Research Objectives and Approach**

To test methodologies for CO<sub>2</sub> storage evaluation using shallow aquifers, we targeted a potable water source (Dockum aquifer) above a long-duration (>35 years) large-scale (~250 km<sup>2</sup>) engineered CO<sub>2</sub> injection site in west Texas. The SACROC oil field in Scurry County, TX, currently operated by Kinder Morgan has injected CO<sub>2</sub> for enhanced oil recovery (EOR) since 1972 with approximately 50% recovery and recycling of injected CO<sub>2</sub>. This site provides the opportunity to investigate (1) if CO<sub>2</sub> from over 35 years of injection can be identified in the shallow aquifer and (2) if groundwater chemistry can be effectively used as a monitoring tool at sequestration sites.

To accomplish our objectives, we compared the groundwater geochemistry of samples collected in the area of CO<sub>2</sub> injection (inside SACROC) to that of groundwater samples collected from areas that have not experienced CO<sub>2</sub> injection (outside SACROC). In addition, we utilize regional historical data from the Texas Water Development Board (TWDB) collected either prior to or spatially removed from any influence of engineered CO<sub>2</sub> injection from the SACROC or nearby Sharon Ridge Field to establish regional background variability in geochemistry. Geochemical perturbations lying outside the normal range of groundwater variability could signal anthropogenic CO<sub>2</sub> input. In addition, we use stable carbon isotopes to source-identify dissolved CO<sub>2</sub> to distinguish natural microbial inputs from anthropogenic ones.

## Methods

Approximately 113 fresh to slightly saline groundwater samples within Triassic-age Dockum and 8 samples from Permian-age evaporite deposits were collected from 60 private water wells (50- to 500-ft-deep) and 1 spring during five water sampling trips, June 2006 - November 2008. Samples were analyzed in the field for alkalinity, dissolved oxygen, conductivity, pH, and temperature and in the laboratory for major cations and anions, trace elements,  $\delta^{13}\text{C}$ ,  $^{18}\text{O}$ , and  $^2\text{H}$  isotopes, dissolved organic and inorganic carbon, and headspace gases. Ten samples of brines co-produced by Kinder Morgan from the 6,000- to 7,000-ft injection/production zone were also analyzed for these parameters. Additional geochemical data on co-produced brines were provided by Kinder Morgan and historical records for Dockum and Permian water geochemistry collected by the Texas Water Development Board between 1936 and 2008 from eight Texas counties were also added to the data set. Carbon isotopes of  $\text{CO}_2$  being injected for enhanced oil recovery, soil organic matter, and soil carbonate from Dockum cores were collected and analyzed for  $\delta^{13}\text{C}$ . Two samples of Dockum core from depth intervals of 450-460 ft and 370-380 ft were examined for mineralogy using SEM with aid of an energy dispersive X-ray system which can identify chemical composition of point area.

## Results and Discussion

Consideration of regional geology and stratigraphy of the area, geochemical trends of collected data, and past and present farming and pre- $\text{CO}_2$ -EOR practices, was used to identify background geochemical influences on Dockum geochemistry. The major influences are; 1) mixing of Dockum groundwater with underlying Permian evaporite waters along a well-documented Permian dissolution zone (i.e., Dutton, 1989), 2) leaching into the Dockum of historically-produced brine formerly stored in unlined surface pits, 3) temporal geochemical variations related to Dockum aquifer pumping and local irrigation practices, 4) groundwater interaction with spatially and compositionally variable stratigraphic units, 5) cation exchange, and 6) dedolomitization. Potential sources of  $\text{CO}_2$  in Dockum groundwater were identified as; 1)  $\text{CO}_2$  injected into the production zone, 2)  $\text{CO}_2$  produced from microbial activities, and 3) degassing from rock-water reactions.

The findings at SACROC are pertinent to a wide variety of hydrogeologic environments where GS sites may be implemented and therefore must be considered when developing a near-surface monitoring program. They illustrate the importance of understanding hydrochemical context and background variability to implementing monitoring protocol. These points are further illustrated below:

- 1. Geochemical Context** - The geochemical driving forces of the hydrochemical system must be defined before the consequences of  $\text{CO}_2$  input can be predicted. In the Dockum aquifer, as well as in many other aquifers, mixing of concentrated waters (in this case Na-Cl brines with cation exchange and  $\text{Ca-SO}_4$  Permian evaporite waters) drives dedolomitization. Dissolution of dolomite and precipitation of calcite (dedolomitization) fueled by calcium ions is widely documented and common in many hydrologic systems (Pacheco and Szocs, 2006; Back and Baedeker, 1989; Back et. al., 1979; Plummer and Back, 1980; Hanshaw and Back, 1985) and creates a significantly different carbonate environment than that of

simple calcite dissolution. Whereby calcite dissolution is driven by  $\text{CO}_2$ , dedolomitization is driven by calcium ions which create undersaturation of the system with respect to dolomite and oversaturation with respect to calcite. Input of  $\text{CO}_2$  into these very different systems has been modeled to produce very different outcomes. In the simple system, DIC increases with increases in the partial pressures of  $\text{CO}_2$  ( $\text{PCO}_2$ ) as previous researchers have predicted. However, in the case of dedolomitization, evolution of groundwater proceeds towards lower  $\text{HCO}_3^-$  concentrations. Increases in  $\text{PCO}_2$  simply shift this overall trend towards higher  $\text{HCO}_3^-$  but retain the same overall evolutionary trajectories. This complex geochemical reaction would yield inaccurate conclusions if dedolomitization had not been identified as a dominant process.

- 2. Background variability** - Because  $\text{CO}_2$  exists naturally in an aquifer, stable carbon isotopes were used to determine if exogenous  $\text{CO}_2$  in the Dockum aquifer could be distinguished from natural  $\text{CO}_2$ . Stable carbon isotope ratios of various carbon sources in the system, the PHREEQC numerical code, and isotope mass balance equations were used to; 1) model isotopic trends during dedolomitization under open and closed systems and, 2) identify the most likely source of  $\text{CO}_2$  in the Dockum aquifer. We modeled carbon isotopic and DIC trends during dedolomitization in open- and closed-systems with and without injectate and microbial  $\text{CO}_2$  input. Whereas isotopic trends for calcite dissolution are straightforward, isotopic trends during dedolomitization are complex. When coupled with high background geochemical variability such as in the Dockum aquifer system, stable carbon isotopes do not yield definitive results. Hence stable carbon isotopes do not appear to be the best tool for positive identification of injectate  $\text{CO}_2$  in the Dockum aquifer – and possibly in other complex aquifer systems as well.

## Conclusions

Based on a field study and modeling of a long-running, large-scale engineered  $\text{CO}_2$ -EOR site, we conclude that shallow aquifer geochemistry has limited applicability for monitoring permanence of  $\text{CO}_2$  storage at GS sites. Many natural and man-induced factors create hydrochemical variability that may mask the effects of  $\text{CO}_2$  input in common hydrogeologic environments. Detailed costly studies of each geochemical system would be necessary to assure that interpretations are correct. Assumptions about  $\text{CO}_2$  leakage formed by observation of geochemical parameters without knowledge of controlling geochemical processes would lead to incorrect conclusions.

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