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2 **Comparison of geochemical data obtained using four brine**
3 **sampling methods at the SECARB Phase III Anthropogenic Test**
4 **CO₂ injection site, Citronelle Oil Field, Alabama**

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ABSTRACT

The chemical composition of formation water and associated gases from the lower Cretaceous Paluxy Formation was determined using four different sampling methods at a characterization well in the Citronelle Oil Field, Alabama, as part of the Southeast Regional Carbon Sequestration Partnership (SECARB) Phase III Anthropogenic Test, which is an integrated carbon capture and storage project. In this study, formation water and gas samples were obtained from well D-9-8 #2 at Citronelle using gas lift, electric submersible pump, U-tube, and a downhole vacuum sampler (VS) and subjected to both field and laboratory analyses. Field chemical analyses included electrical conductivity, dissolved sulfide concentration, alkalinity, and pH; laboratory analyses included major, minor and trace elements, dissolved carbon, volatile fatty acids, free and dissolved gas species. The formation water obtained from this well is a Na-Ca-Cl-type brine with a salinity of about 200,000 mg/L total dissolved solids. Differences were evident between sampling methodologies, particularly in pH, Fe and alkalinity. There was little gas in samples, and gas composition results were strongly influenced by sampling methods. The results of the comparison demonstrate the difficulty and importance of preserving volatile analytes in samples, with the VS and U-tube system performing most favorably in this aspect.

Keywords: Brine; Carbon capture and storage; Produced water; U-tube; Wireline fluid sampling

1. Introduction

Accurate measurements of the chemical composition of deep groundwater or formation water, including dissolved gases, and gas samples is essential in understanding subsurface geochemical processes caused by CO₂ injection to enhance oil recovery (EOR) and the geologic sequestration of CO₂. In addition, monitoring CO₂ injection for verification and detection of CO₂ migration and leakage is a critical part of any geologic CO₂ storage project (Friedmann, 2007; Harvey et al., 2013; Kharaka et al., 2013). Groundwater samples collected from deep, saturated formations under moderate to high hydrostatic pressures will undergo significant pressure and temperature changes when the samples are brought to the ground surface. The dramatic change in sample conditions can result in the loss of volatile components, changing groundwater chemistry, especially through changes in pH and saturation states (Wolff-Boenisch and Evans, 2014). This work primarily investigates four different sampling methods (gas lift, electric submersible pump, downhole vacuum sampler, and U-tube) to obtain representative saline water samples from the Paluxy Formation produced from SECARB characterization well D-9-8 #2, which is a well permitted for experimental technology testing that is located in Citronelle Oil Field in Mobile County, Alabama.

1.1 Overview of water sampling techniques

There are many techniques available for sampling deep fluids (Wolff-Boenisch and Evans, 2014), which include *in situ* downhole methods such as positive displacement samplers, vacuum samplers, and flow through samplers, and also *ex situ* uphole methods, such as pumps, the U-tube sampler, and other production string sampling. Accurate measurement of pH and volatile species when using surface samples is of concern, so techniques that maintain *in situ*

conditions are a better approach for higher fidelity data. Nonetheless, many times sampling takes place at the wellhead rather than downhole, and thus samples are subjected to reductions in temperature and pressure, to gas loss and to exposure to oxidizing conditions (Kharaka and Hanor, 2014). Drilling and circulation fluids can mix with native formation groundwater when a well is installed, which can also affect sample quality and subsequent geochemical interpretations. Tracers including Rhodamine WT, and fluorescein, or natural chemical components, such as chloride or bromide, can be used to tag fluids introduced into the well, allowing for identification of non-native formation water (Kharaka et al., 2006b). For detailed geochemical investigations such as the CO₂ injection study at Frio, Texas, tracer gases including SF₆, noble gases, tagged CH₄, and perfluorocarbons (PFTs) were injected with the CO₂ to map its flow path in the reservoir sandstone and identify any leakages into the overlying sandstones and shallow groundwater (Kharaka et al., 2009). Conditioning a well before geochemical sampling is another important consideration, which can be done by producing several well volumes of fluid before attempting to take representative samples. The sampling methods used in the present study are summarized on Table 1 and described in detail below.

Gas lift is a commonly used technique to raise formation fluids for sampling. Gas lift injects pressurized gas into the well, reducing the density of the wellbore fluid, and stimulating flow driven by the pressure in the formation. Before geochemical sampling, gas lift can be used in the well conditioning process for cleanup by flowing the well to remove residual drilling or workover fluids. This technique produces large brine volumes, but unintended effects may occur, such as the removal of volatile components including dissolved CO₂ that could raise pH causing mineral-solution disequilibrium, mineral precipitation, and other chemical changes.

There are many studies illustrating these effects in typical groundwater sampling (Barcelona, 1990; Parker, 1994; Schuller et al., 1981; Stolzenburg and Nichols, 1985).

Another common technique for sampling includes the pumping of formation fluid via electric submersible pump (ESP). These pumps have a centrifugal pump above a sealed motor and are lowered into the well and push fluids to the surface. An ESP can be used in well conditioning and produces large fluid volumes. Similar to gas lift however, dissolved volatiles and gases can be lost during pumping, thus raising pH and causing mineral precipitation and other chemical changes. Likewise, there are a number of studies illustrating these changes in typical groundwater applications (Barcelona, 1990; Parker, 1994; Stolzenburg and Nichols, 1985).

Directly sampling fluids with a downhole tool is another strategy for sampling formation water. Many such technologies are available (Wolff-Boenisch and Evans, 2014), and they generally are wireline or slickline-based tools designed to keep a fluid sample at *in situ* formation pressure conditions until it can be processed at the surface. This study employed a commercially available (Kuster Company, Long Beach, CA) downhole vacuum sampler (VS), also called a closed chamber sampler, that is lowered into the well with a slickline. This tool consists of a sample bottle with an inlet valve, two non-return valves, locking device, and timer. The sampler can be cleaned and evacuated, minimizing contamination, and placed at any depth in the well. It has a small surface area for reaction and brine and gas can be sampled at *in situ* conditions; but it requires a trained operator, can have a moderate rate of deployment failure (Fisher and Becker, 1993), and has a small sampling volume (~1 L). Because of the small volume sampled, this technique cannot be used to purge a well prior to sampling, and gas lift or pumping are required to adequately purge the well.

The U-tube sampler, described in detail by Freifeld et al. (2005), is in essence a fixed loop of narrow (6 mm or 9 mm diameter) stainless steel sample tubing extending from the surface to the sampling depth of interest and back that is coupled with a positive pressure fluid displacement pump using high pressure gas, usually N₂, or water drive. The U-tube sample tubing is fixed in the well, typically attached to the outside of production tubing string, and samples an area isolated by a packer. Compared to the downhole VS and other similar tools, the U-tube samples a larger volume (tens of Ls), is at high pressure at surface, and once installed, it is easier to operate. Because the U-tube sampler is fixed in place, its sample tubing can be contaminated with prior-sampled brine, N₂, and organics, and its operation is fixed at one depth. Additionally, due to sample transport inside narrow steel tubes away from the wellhead, fluid samples are substantially cooler than the formation temperature.

Prior sampling at the Frio Brine Pilot experiment, where the U-tube was first tested in the field, showed sample chemistry from the U-tube and the VS were similar, so subsequent simultaneous sampling using the two methods was considered redundant (Freifeld et al., 2005). Later, more detailed chemical analysis, including gases and trace and volatile components were observed to be different using the two methods at Frio (Kharaka et al., 2006a; Kharaka et al., 2009). These differences were confirmed and subsequently observed at another SECARB research location, the Cranfield EOR site. Both the U-tube and the VS were used to sample Tuscaloosa Formation fluid in Cranfield oilfield, Mississippi. Differences in brine chemistry were noted and attributed to the various sampling methods (Lu et al., 2012). Unfortunately, due to the similarity of sampling method results at Frio, the sampling procedure at Cranfield was not designed to test these sampling methods. The use of both methods was fortuitous because the

narrow steel tubing of the U-tube sampler was blocked temporarily, and the VS was used as an alternative sampling method.

1.2 Background on Citronelle Oil Field and SECARB project

The geology and history of the Citronelle Oil Field was described by Eaves (1976) and more recently by others (Esposito et al., 2010; Esposito et al., 2011; Koperna et al., 2013). The region is part of the Mississippi Interior Salt Basin, and the Citronelle area is characterized by a broad anticline present in the Jurassic through Quaternary strata that was created by deformation from a salt dome forming from the Louann Salt. The opportunities at the Citronelle Oil Field for carbon storage and enhanced oil recovery are described by Esposito et al. (2010), and the Citronelle Dome is recognized as a major potential geologic storage area for CO₂ and an excellent target for EOR.

Developing CO₂ monitoring, verification and accounting tools and protocols is a critical part of any carbon capture and storage technology (IEA, 2013). The Citronelle injection site is part of the SECARB Anthropogenic Test project, described by Esposito et al. (2011) and Koperna et al. (2013), which is an integrated pilot project for CO₂ capture, transport and storage. The capture of CO₂ occurs at the James M. Barry Electric Generating Plant in Bucks, Alabama. The plant has 7 generating units, including both coal and natural gas-fired units. The CO₂ capture technology is post-combustion capture from a coal-fired unit where combustion flue gases are first cooled and then react with amine solvent in an absorber unit. The CO₂ is then stripped from the solvent, compressed to a supercritical fluid, and transported 19 km by pipeline to the injection site at Citronelle. Three wells were drilled at the Citronelle site as an initial part of the project: a primary CO₂ injection well (D-9-7#2), a backup injection well (D-9-9 #2), and a characterization well (D-9-8 #2). Each well was drilled to a depth of ~3597 meters, the base of

the oil-producing “Donovan Sand” (the wells are designed to be used later for oil production operations). The injector well is perforated between 2865 to 3048 m, designed to introduce supercritical CO₂ into fluvial sandstones of the Paluxy Formation containing saline groundwater. The injection of CO₂ began in August 2012 and concluded in September 2014 after injecting 114,104 metric tons.

2. Methods

2.1 Brine and gas sampling

The sampling and methods used in this study, as detailed elsewhere (Lico et al., 1982) and summarized below, are similar to previous field work at Cranfield CO₂ sequestration site, Mississippi, USA (Lu et al., 2012), and Frio Brine pilot tests, Texas, USA (Kharaka et al., 2006a; Kharaka et al., 2006b; Kharaka et al., 2007; Kharaka et al., 2009). The D-9-8 #2 characterization well is drilled to a depth of 3597 m and perforated between 2866–2875 m. This characterization well was sampled in March and June of 2012 (Table 2). During or prior to each of these two sampling periods, coiled tubing was used to condition the full length of the well using gas lift, cleaning the well from drilling fluids and KCl solutions, producing at least three well volumes of formation water, which was considered sufficient to obtain a representative sample. Conductivity was monitored for the development of a consistent value to ensure representative formation water was being produced (Figure 1). *In situ* temperature and pressure as determined by a sensor associated with the U-tube were about 106.5 °C and 30 MPa.

Brine sampling using gas lift was performed in both March and June of 2012. Samples were taken after the well was conditioned, and water quality was monitored for electrical conductivity as before. Samples were collected from the flowline at the wellhead. The ESP

samples were taken in March 2012. The ESP was lowered to a depth of 213 m, and the water level in the well before sampling was about 69 m. Samples were collected from a flow line at the wellhead. The VS was used in both March and June of 2012, and lowered to a depth of about 2834 m, which is about 32 m above the perforations. The U-tube was installed between March and June 2012, and U-tube samples for this study were obtained in June 2012. Because of the depth of the sampling interval and the density of the brine, the sample column was too heavy to drive using N₂ pressure alone, so local groundwater was used as a drive fluid until the sample column was light enough to drive with N₂. In addition to 2012 sampling, two U-tube samples were collected in May 2013.

The composition of gas evolved from pressurized samples was determined on samples collected in 2012 using the VS in March and June, and the U-tube in June. Gas samples were collected in low-carbon austenitic stainless steel sampling cylinders (Swagelok®), typically with a 75 or 300 mL volume. The cylinders were attached to the U-tube sampling manifold, or a custom-built gas manifold to interface with the VS. Gas samples from the VS were collected into pre-evacuated cylinders, and U-tube samples were collected using both flow through and pre-evacuated techniques. Additional gas samples (12-CIT-G1, -G2) were collected from the annulus at the wellhead using a flow-through technique. After sampling (and at ambient conditions), the cylinders typically contained both a brine and gas phase. The volume and mass of brine obtained were determined analytically, and the gas headspace determined by difference using the cylinder size. Pressure in gas cylinders for the VS and wellhead samples were lower (<30 kPa) than atmospheric pressure after collection, whereas pressure in cylinders from U-tube sampling was 10–20 MPa, and as mentioned above the *in situ* pressure was 30 MPa.

2.2 Sample handling and analysis

Sample handling and analysis conducted in this study follows protocols described in Kharaka and Hanor (2014). Raw water samples from well-head, U-tube manifold, or downhole sampling tools were collected in either 2-gallon polyethylene carboy or 1-L wide-mouth polyethylene bottle. Electrical conductivity on raw water samples was measured on site at the time of collection using a Thermo Orion Research Model 128 conductivity meter, and repeated in the laboratory when samples had cooled to ambient temperature (20 °C). For the analysis of pH, alkalinity, ammonia, and dissolved sulfide, the raw water collection bottle was used to pre-rinse and fill 125 mL narrow mouth glass bottles with no head space and a Polyseal cap. Temperature and pH were determined using an Orion 250A+ portable pH meter on raw water samples shortly after collection using Orion 9107 BN triode probe calibrated against 0.05M buffer solutions. Alkalinity and dissolved sulfide concentration were determined immediately on site by titration using burets and volumetric pipettes. Although alkalinity determinations are often performed on filtered water samples (Rounds, 2012), in geopressurized and oil-field waters it is common practice to make these determinations using unfiltered (“raw”) samples (Kharaka and Hanor, 2014; Lico et al., 1982), as we have in this study. Moreover, there was little observable suspended material in samples. Alkalinity was titrated for using precalibrated 0.05 N sulfuric acid, and results are reported using the inflection point method (Rounds, 2012). Because of the difficulty in determining pH in very high ionic strength samples (> 20 mS/cm) and the associated uncertainty in alkalinity results, both pH and alkalinity values should be treated as estimates in this study. Dissolved sulfide was determined by iodometric titration using a starch indicator. For the analysis of ammonia, the raw water collection bottle was used to pre-rinse and fill 125 mL narrow mouth glass bottles with no head space and a Polyseal cap. Samples for the analysis of ammonia were chilled and returned to the laboratory where concentrations were

determined using an ion selective electrode. Filtered water samples were collected using aliquots from the raw collection bottle syringe passed through either 0.1 or 0.45 μm syringe filter (Gelman Supor polyethersulfone low extractable filters).

For cation analysis, filtered samples were acidified in the field with 4–6 drops of concentrated nitric acid (Fisher Optima grade) to pH 1.0–1.5. Cations and trace metals were then determined in the laboratory using ICP-MS (Perkin-Elmer ELAN 6000). Samples were diluted to below 1000 mg/L total dissolved solids (TDS) as estimated from electrical conductivity, and calibration performed using internal standards method to minimize for matrix effects. Relative standard deviation of results for duplicate samples ($n = 2$) was typically better than 6% for analytes. Charge balances were calculated with respect to anion concentrations as a further data quality check, and sample results with poor charge balance ($<97\%$) were reanalyzed.

For anion analysis, samples were collected into 60 mL HDPE bottles pre-rinsed with deionized (DI) water and dried. Anions were analyzed on a Dionex DX-500 ion chromatography system using an AS4-A column with an eluent of 1.7 mM sodium bicarbonate/1.8 mM sodium carbonate and a self-regenerating suppressor. Relative standard deviation of results for duplicate samples ($n = 2$) was typically better than 1% for analytes.

Filtered samples for measurement of volatile fatty acids (VFAs) were collected into pre-cleaned 40 mL amber glass vials (I-CHEM) with Teflon-faced silicone septa. These samples were preserved in the field by the addition of 160 μL of a 10 mg/mL mercuric chloride solution. After returning to the laboratory, samples were diluted 1:5 and extracted using Dionex OnGuard II Silver cartridges to remove excess chloride. Extracted waters were then analyzed by high-performance ion chromatography (HP-ICE) on a Dionex DX-500 ion chromatography system

using an AS-1 column with an eluent of 1.0 mM octanesulfonic acid in 2% isopropanol and using 5.0 mM tetrabutyl ammonium hydroxide as a chemical suppressor.

Similar to samples for VFAs, filtered samples for dissolved organic carbon (DOC) analyses were collected into pre-cleaned 40 mL amber glass vials with Teflon faced silicone septa and preserved by the addition of 160 μ L of a 10 mg/mL mercuric chloride solution. Because of high salinity, samples were diluted 1:5. Samples were then analyzed by high-temperature catalytic oxidation (HTC-TOC, Shimadzu Inc.).

For the analysis of dissolved inorganic carbon isotopic composition ($\delta^{13}\text{C}$ -DIC), the raw water collection bottle was used to pre-rinse and fill 125 mL glass bottles with no head space and a Polyseal cap. Precipitation of dissolved carbonate species was performed using a method similar to that outlined by Bishop (1990). Shortly after collection, precipitation of dissolved carbonate species was performed by adding 5 mL of SrCl_2 -saturated ammonium hydroxide. Bottles were shaken and allowed to precipitate for >48 h. To filter precipitate, bottles were again shaken and about 10 mL of precipitate slurry was filtered using a glass fiber filter paper in a Swinnex® filter holder. Precipitate was rinsed on the filter in the holder using vacuum-degassed ultrapure water until the pH of the filtrate had a neutral pH. The filter with precipitate was then dried in an oven at 80 °C for 4–8 h. Precipitate was scraped off the filter paper, and disaggregated, and 1–3 mg placed into a pressed tin capsule. Samples were then analyzed using combustion-interfaced cavity ring-down spectroscopy (CRDS). For samples collected in 2013, DIC and $\delta^{13}\text{C}$ -DIC were performed using a total organic carbon analyzer (OI Aurora 1030W) coupled with a CRDS (Picarro G2101) in a continuous flow configuration (Conaway et al., 2015). All carbon stable isotope ratios are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard.

The activity of ^{226}Ra in a subset of samplers was determined using an ultra-low background high-purity germanium (HPGe) well detector measuring 352 and 609 keV γ -ray emissions. Acidified sample water was transferred to a 10 mL γ -ray counting vial and sealed, then analyzed. Reported uncertainties reflect propagated errors arising from 1- σ counting error, the detector efficiency calibrations, and the background correction. The detector time per sample (count time) was 1 day.

Gas samples in cylinders under partial vacuum was extracted using a mercury manometer apparatus; for cylinders at greater than atmospheric pressure, gas was extracted using an additional cylinder for volume expansion. The extracted gas was analyzed for He, H₂, Ar, O₂, N₂, CH₄, CO₂, C₂H₆, H₂S, CO, C₃H₈, C₄H₁₀, iso-C₄H₁₀, and C₂H₄ gases using a Perkin-Elmer gas chromatograph with a dual-injection system using Ar and He carrier gases. Results for these analytes were normalized to 100% volume. Data were then corrected for partitioning between headspace and brine in cylinders (if any) using our data for brine chemistry (i.e., TDS), calculated pressure and headspace, and equations outlined by Barton and Chou (1993) for CO₂, Crozier and Yamamoto (1974) for H₂, Weiss (1970) for O₂ and N₂, and Drummond (1981) for CH₄ and other gases.

3. Results and Discussion

3.1 Brine chemistry

A preliminary examination of the data was performed to identify samples that were influenced to various extents by drilling, workover, or other fluids. First, conservative elements sodium and bromine (Na, Br) and TDS were examined relative to potassium (K), which is a good indicator of contamination of native groundwater by well workover fluids containing KCl that

284 were employed at Citronelle. This examination was performed by plotting bromide versus the
285 ratio of cations Na^+ and K^+ (Figure 2). In sample 12-CIT-100, which represents the first sample
286 collected from the well (using N_2 lift), K^+ was the predominant dissolved cation and there was
287 low TDS (37 g/L), demonstrating the sample is mostly a KCl solution (the sample is roughly 3%
288 w/v KCl). In addition, 12-CIT-106, -107, -222, and -224, which represent the first two ESP
289 samples and both U-tube samples, have relatively low ratio of Na to K (Na:K 42–66 mass ratio)
290 and low TDS (≤ 190 g/L) when compared to other samples (Na:K average $\pm 1\sigma$ is 70.7 ± 0.7 ;
291 TDS average 200 ± 2 g/L). A second test of 2012 brine data (excluding 12-CIT-100) was
292 performed by graphical examination of normal probability plots of individual cation and anion
293 species. Although there are too few samples ($n = 16$) for many types of statistical testing, data
294 distribution appeared normal, although one U-tube sample (12-CIT-224) appeared as an outlier
295 for many analytes, which was confirmed as statistically significant ($p < 0.05$) in most cases using
296 Grubbs' test. A third approach using a correlation matrix of both cation and anion identified Na
297 and Sr concentrations as highly correlated ($r = 0.9$), suggesting conservative mixing of the brine
298 with another source of fluid. Furthermore, the lowest concentrations of Na and Sr were
299 associated with lowest Ba and highest SO_4 concentrations (Tables 3 and 4), and these
300 observations were made in early gas lift samples (12-CIT-101, -102), initial ESP samples (-106,
301 -107), and U-tube sample -224, suggesting barite saturation plays a role in the chemistry of the
302 non-native or modified fluid that is mixing with the native brine. Taken together, these three
303 initial tests suggest some influence of drilling or other fluids in early gas lift and ESP samples, as
304 well as in U-tube sample -224, although in each case samples are still predominantly formation
305 brine.

Following the initial screening of data for contamination, the basic physical and chemical properties of the brine were examined. As expected, the samples were highly saline, and field-determined electrical conductivity of 2012 brine samples had an average value ($\pm 1\sigma$) of 191 ± 5 mS/cm (Table 2). Laboratory-based determinations of conductivity, where sample temperatures were all about 20 °C, showed consistent range of conductivity values (200 ± 3 mS/cm). The difference of laboratory versus field-determined conductivity was demonstrated to be a result of the instrument's temperature correction algorithm (data not shown), which does not adequately account for sample chemistry, and thus laboratory-based measurements were deemed higher quality for intercomparison. Field measurements of pH ranged 5.3–6.5, and were generally lowest in VS samples and highest in gas-lift collected samples (see methods comparison discussion below). It is important to emphasize that these field determined pH and T values do not represent *in situ* conditions, although the data are useful in reconstructing such conditions or in understanding geochemical changes during the sampling process, such as the loss of CO₂.

The predominant cations in the formation water are Na⁺ and Ca⁺ (Table 3), with Na representing about 23% of total dissolved solids (TDS) by mass, and Ca 13%. The waters are therefore Na-Ca-Cl type brines. Na⁺ represents about 58% of the cation electrical charge (meq/L). The range of [Na⁺] observed in samples (41,800–48,800 mg/L) is somewhat lower than that (53,100–69,300 mg/L) observed in metal-rich brines from central Mississippi Salt Dome basin (Kharaka et al., 1987), and the Na fraction of the total cations by mass (60%) is somewhat less than that generally observed in oil-field waters, which is 70% to >90% (Kharaka and Hanor, 2014). The concentration of trace metals in samples is generally low, consistent with observations made in basinal brines elsewhere (Hitchon et al., 2001; Kharaka and Hanor, 2014; Kharaka and Thordsen, 1992), except where there was the possibility of contamination from

sampling tools, such as Pb and Cu in the VS (discussed below). The predominant anion in the formation water is Cl^- , representing 62% of TDS by mass (Table 4). Cl^- represents about 99% of the anion electrical charge. The distribution of Cl and Br in samples (Figure 3) shows Br:Cl ratios that plot below the evaporation line for seawater (i.e., Br enriched), which can be interpreted as a mixture of highly evaporated seawater or bittern with either fresh water or less evaporated seawater (Engle and Rowan, 2013; Kharaka and Hanor, 2014). Total dissolved solids (TDS), calculated as the sum of all cations and anions, including estimated carbonate species and VFAs (discussed below), ranged from 196–204 g/L, with an average $\pm 1\sigma$ of 200 ± 2 g/L (Table 2).

Alkalinity of 2012 brine samples from the characterization well ranged 78–270 mg/L as HCO_3^- (Table 5), equivalent to about 1.3–4.5 meq/L. The carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$) ranged from -11 to -20‰. These alkalinity results were highly dependent on the sampling method used (see methods comparison discussion below). The most representative values, collected using the VS, are in the range of 150–220 mg/L as HCO_3^- and $\delta^{13}\text{C-DIC}$ of -18‰. Although alkalinity data for D-9-8 #2 samples collected in 2013 are within the ranges observed in 2012, the 2013 samples tend to have lower alkalinity and higher surface measured pH (Figure 4). Only one sample was analyzed for $\delta^{13}\text{C-DIC}$ in 2013, but the result -8.4‰ was notably more enriched than results for 2012.

The presence of high concentrations of naturally occurring radioactive material (^{226}Ra concentration 1600–1700 pCi/L; Table 5) in samples is consistent with observations for high-salinity produced and formation water elsewhere, particularly those from the Texas and Louisiana Gulf Coast (Fisher, 1998; Kraemer and Kharaka, 1986; Kraemer and Reid, 1984).

There was no detectable dissolved sulfide (> 1 mg/L) in any sample where it was measured (Table 5). This is consistent with low concentration of dissolved sulfide observed in many clastic sedimentary sequences where iron-bearing mineral phases are abundant and dissolved sulfide is below the limit of detection (Kharaka and Hanor, 2014; Kharaka et al., 1987).

Acetate was the predominant VFA detected, with an observed concentration of 1.0–3.8 mg/L in 2012 samples, average 1.8 mg/L (Table 6). The DOC concentration measured by HTC-TOC was 2.9–28 mg C/L, with a median of 6.0 mg C/L, whereas the fraction of DOC represented by the sum of VFAs detected by HP-ICE, including acetate, was 0.2–1.3 mg C/L. These VFA and DOC concentrations are relatively low compared to that observed in many metal-rich brines from central Mississippi Salt Dome basin (Kharaka et al., 1987), and much lower than maximum reported or likely values for oil-field waters (Kharaka and Hanor, 2014; MacGowan and Surdam, 1990). The potential contribution of VFAs as a neutralizing species in alkalinity titrations is about 0.03 meq/L, typically about 1% of the alkalinity in samples. Relatively high DOC results in some samples, 12-CIT-106, -107, and -224, suggests possible contamination (discussed below in Methods Comparison).

Most parameters in samples collected in 2013, including initial pH, TDS, Cl, SO_4 , B, K, Li, Ca, Sr, Mn, Zn are generally consistent with 2012 samplings. Some 2013 results were somewhat higher than 2012 results, such as for Mg and Br (about 10% higher), and Ba in 13-CIT-103 (about half of the 2012 concentration). In contrast, Fe was much higher in 2013 samples, roughly 300 mg/L in 2013 compared to 120 mg/L in 2012. This difference may indicate that Fe concentrations are substantially influenced by the sampler condition and the well material itself.

3.2 Methods Comparison for Brine Chemistry

As shown in the results described above, there are differences in physical and chemical results for brine properties that are related to sampling method, particularly related to carbonate system chemistry and trace metals. This section summarizes the differences observed in each method, and discusses these differences in relation to loss of volatile components and contamination of trace elements.

As previously mentioned, surface measured pH values (Table 2, Figure 4) were generally highest with gas lift collected samples (pH 6.4–6.6), which suggests a loss of dissolved CO₂ (i.e., dissolved carbonic acid). This explanation is supported by the $\delta^{13}\text{C}$ -DIC data plot (lower panel), which show that gas lift samples are typically more enriched ($\delta^{13}\text{C}$ -11 to -13‰) than other samples (about -15 to -20‰) possibly resulting from fractionation associated with CO₂ degassing from the brine. Samples with higher surface measured pH, such as the gas lift samples, also tended to have lower alkalinity. Loss of CO₂ should not affect alkalinity except through pH-driven precipitation or dissolution reactions (Stumm and Morgan, 1996). Thus we tentatively attribute the loss of alkalinity in higher pH samples to the precipitation of calcite (CaCO₃). Although gas data are not of sufficient quality for detailed geochemical modeling (see below), calculations of solution composition of samples at in situ temperature and pressure using SOLMINEQ.88 (Kharaka et al., 1988) show that gas lift samples are substantially more saturated with respect to calcite compared to other sampling methods, which is consistent with a loss of alkalinity via calcite precipitation in the gas lift sampling process. This precipitation would cause a small change in dissolved Ca (roughly 100 mg/L) relative to its total concentration in the brine (25,000 mg/L), and would therefore not likely be observable in the Ca results. Despite the differences in the pH and alkalinity between gas lift and other sampling methods, for most major anions, cations, DOC, and other solutes the gas lift sample results are generally consistent with

the results of other methods. This suggests that use of this sampling method should be limited to major and unreactive solutes.

The results for the ESP samples were variable and showed evidence of both contamination and loss of volatiles. This is unsurprising given setting depth of the pump (213 m), which the results demonstrate is too shallow for adequate sampling. Proper setting depth of the pump has shown to be important in avoiding degassing or cavitation in the fluid, and associated precipitation of minerals, which is important both in obtaining samples for chemical analysis, but also to protect the pump itself from clogging and damage (Aksoy, 2007; Wolff-Boenisch and Evans, 2014). Samples taken by ESP had high iron concentrations (61–77 mg/L) relative to other sampling methods, which have a range of 18–39 mg/L (excluding sample 12-CIT-100), showing contamination from the well. (Table 3). In addition, the first two collected ESP samples (12-CIT-106 and -107), were relatively low in Cl and high in DOC concentrations (12–13 mg C/L; Table 6), and a low-carbonate along with high pH (Figure 4), showing contamination by other fluids and organic sources besides formation water as well as potential loss of dissolved CO₂. These results suggest that with care and proper setting depth, ESP samples can be used for major and unreactive solutes, but that the potential for loss of volatiles and contamination for trace metals and organics can be high.

The results for samples collected using the VS were generally consistent with each other, and showed little evidence for loss of dissolved gas or contamination of organic carbon. Field measurements of pH were lowest with VS samples (5.3–5.7) compared to other samples (Table 2). The VS samples also showed a relatively low range of $\delta^{13}\text{C-DIC}$ results ($-17.6 \pm 0.2\text{‰}$) compared to $\delta^{13}\text{C-DIC}$ variability in other sampling method results (Table 5, Figure 4). In addition, the results from the VS samples were generally consistent with the results from other

sampling methods when they had minimal evidence of contamination or loss of volatiles. As discussed above, VS samples showed high concentrations of copper (0.79–4.4 mg/L) compared to other methods, and occasional high lead concentrations (9.0–9.6 mg/L), which we tentatively attribute to sampler contamination related to sealants or lubricants for threads and O-rings, although one high copper concentration (8.0 mg/L) was observed in U-tube sample 12-CIT-222, which had a high lead concentration as well (7.3 mg/L). These results show that the VS used generates the most consistent results for most analytes, including dissolved CO₂, but care should be taken to minimize the sources of contamination.

The results from the first U-tube collected sample (12-CIT-222) are generally similar to results from the VS. This is consistent with previous observations at Frio Brine Pilot experiment, where little difference was observed between VS and U-tube results (Freifeld et al., 2005). Despite these general similarities, alkalinity in 12-CIT-222 (270 mg/L as HCO₃⁻) was the highest measured for any sampling method in this study, and δ¹³C-DIC (-11.6‰) was similar to those samples collected by gas lift (Figure 4), and somewhat heavier than observed in VS and other sampler methods (generally -15 to -20‰). Relatively low Cl, Br, and relatively high K and DOC in the second U-tube collected sample (12-CIT-224) suggest influence from drilling fluids or workover fluids (Tables 3, 4, and 6).

3.3 Gas Chemistry

An examination of gas data (Table 7) shows that samples were predominantly N₂ (50–80%) and CH₄ (15–32%). These results, however, are indicative of gas contamination from gas lift, the U-tube drive, and atmospheric sources. Either a very high N₂ composition, or a departure of the N₂/Ar ratio from that observed in the atmosphere (roughly 84) suggest contamination by N₂. This N₂ contamination could happen either through the U-tube sample

drive gas, or through gas (N_2) lift performed in the well. The latter is a possibility because the characterization well was purged with coiled tubing gas lift using N_2 , and the formation may have contaminated with N_2 during the time that the coiled tubing was below the perforations, i.e., total depth of 3597 m and perforated between 2866–2875 m. An examination of the N_2 /Ar ratio in gas samples (Figure 5) shows that those collected with the VS have N_2 /Ar ratios (N_2 :Ar 85–115) close to that of the atmospheric ratio (N_2 :Ar 84). U-tube and wellhead collected samples are substantially higher in the ratio, demonstrating excess nitrogen that can be attributed to the U-tube sampling process or gas lift. The presence of residual N_2 is not surprising in U-tube collected samples, and in some cases it is possible to correct for this N_2 in examining gas composition (Freifeld et al., 2005). In this study, quantifying “excess” N_2 from the U-tube is made difficult by the additional source of residual N_2 from gas lift.

Both the presence of O_2 in gas samples and the presence of oxidized iron in brine in gas cylinders are evidence of contamination by ambient air. Samples 12-CIT-109 (VS collected) and -G1 had 2–3% oxygen content. The brine in the 12-CIT-109 cylinder was deeply red-colored by iron oxide sediment, and the brine in 12-CIT-110 (VS) somewhat less colored by iron oxidation. Sample 12-CIT-225 (VS) had very little brine, and consequently no observable oxidized iron. U-tube collected 12-CIT-224 samples showed no evidence of iron oxidation in the brine fraction of the cylinder. Thus, when there is very little evolved gas, residual air in the vacuum chamber and sampling manifold appears to be an important consideration in VS collected samples.

Finally, an examination of N_2 versus CH_4 data (Figure 6) suggests a formation gas that is predominantly CH_4 diluted by air or influenced by N_2 by U-tube sampling or gas lift. The composition of N_2 and CH_4 appear linearly related. Samples that show evidence of O_2 (i.e., ambient air) contamination plot increasingly away from high CH_4 /low N_2 with increasing

indication of O₂ presence (i.e., from slight oxidation of brine, to measurable O₂ in gas). This leads to the overall conclusion that true composition of the formation gas predominantly methane, with the results masked by atmospheric contamination and residual N₂ from gas lift and U-tube cycles. The difficulty in obtaining representative composition of gas evolved from pressurized samples is compounded by the fact that there is very little gas released.

4. Conclusion

This study presents pre-injection geochemistry of fluids obtained from a characterization well at a CO₂ injection site into a saline formation at Citronelle Oil Field, Alabama, and compares four sampling methods for obtaining those fluids. The effects of sampling devices on sample chemistry is well-known in relatively shallow groundwater studies, and the results here are an example of some of these same effects in the context of even greater temperature and pressure effects that are associated with groundwater samples collected from deep, saturated formations. Specifically, the results demonstrate the difficulty of preserving volatile analytes in samples, particularly loss of dissolved carbonate and associated increase of pH and precipitation of minerals, that has been documented in shallow groundwater studies for both gas lift and various kinds of ESP sampling (Barcelona, 1990; Parker, 1994; Schuller et al., 1981; Stolzenburg and Nichols, 1985). Indeed, in a review of sampling tools available for deep wells, Wolff-Boenisch and Evans (2014) pass over gas lift as a sampling method because alteration of physical and chemical properties of samples is so profound. The importance of sampling depth is shown in the results presented here, as evidenced by the shallow setting depth of the ESP and resulting loss of volatiles and increased contamination. Other work has suggested that with careful attention to setting depth and other parameters, ESP may be an effective sampling strategy in liquid-dominated geothermal and groundwater systems with low overall partial gas

pressures (Aksoy, 2007; Wolff-Boenisch and Evans, 2014). In the results presented here, the VS and U-tube system appear to perform most favorably in preserving volatile analytes. Further investigation should be performed in order to resolve sources of Cu and Pb contamination in the VS used in this study.

In addition to the preservation of volatile components, the importance of well conditioning before geochemical sampling is also shown in the results here, as contamination by workover or drilling fluids was evident or possible in the early gas lift samples as well as initial ESP samples. Although gas lift using coiled tubing substantially affected both brine and gas chemistry, it was essential in flowing a large volume of brine and cleaning the full length of the well, particularly given the large volume between the perforations (2866–2875 m) and the bottom of the well (3597 m). Alternatively, the use of an ESP to condition the well would likely be very difficult and expensive.

Because there was little gas evolved from the pressurized samples in this study, the value of those analytical results are limited, but some insight is nonetheless provided for considering sampling methods. The gas composition results samples collected by U-tube and VS are all influenced to some degree by contamination from air and residual N₂ gas from U-tube cycles or gas lift. Residual air in the vacuum chamber and sampling manifold appears to be an important consideration in VS collected samples under these circumstances. Although correction for residual N₂ is a possibility for U-tube samples, as shown elsewhere (Freifeld et al., 2005), multiple sources of N₂ (residual N₂ from both U-tube and gas lift) make such an approach problematic for this study. Additional method comparison studies in systems with a relatively higher dissolved gas fraction would be valuable.

513 **Tables**

514 Table 1: Summary of sampling methods used in this study.
515

Method	Summary of features
gas lift	Injects pressurized gas into the well, reducing the density of the wellbore fluid, and stimulating flow driven by formation pressure. Can be used to clean a well and produces large brine volumes, but it may remove volatile components and raise pH, causing mineral-solution disequilibrium, mineral precipitation and other chemical changes.
electric submersible pump (ESP)	In deep groundwater applications, this is typically a centrifugal pump above a sealed motor that is lowered into the well and pushes fluids to the surface. An ESP can be used to clean the well and produces large fluid volumes, however this method can remove volatile components.
downhole vacuum sampler (VS)	Also called a closed chamber sampler, this tool is lowered into the well with a slickline and consists of a sample bottle with an inlet valve, two non-return valves, locking device, and timer. The sampler can be cleaned and evacuated, minimizing contamination, and placed at any depth in the well, but has a small sampling volume (~1 L). Brine and gas can be sampled at in situ conditions. Requires a trained operator, and can have a moderate rate of deployment failure.
U-tube	A fixed loop of narrow stainless steel sample tubing extending from the surface to the sampling depth of interest and back that is coupled with a positive pressure fluid displacement pump using high pressure gas or water drive. Tubing is fixed in the well, sampling only one depth, typically attached to the outside of production tubing string, and samples an area isolated by a packer. Samples tens of liters, and can take pressurized samples.

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Table 2: Sampling ID; field collected parameters electrical conductivity (σ), temperature, and surface measured pH; and calculated total dissolved solids (TDS) for gas lift, electric submersible pump (ESP), downhole vacuum sampler (VS), and U-tube.

SAMPLE ID	sampling method	date and time ^a mm:dd:yy hh:mm	σ (mS/cm)	σ (mS/cm)	T °C	surface measured	TDS ^d mg/L
			Field ^b	Laboratory ^b		pH ^{c,†}	
12-CIT-100*	gas lift	03/07/12 08:10	61.6	62.3	20.5	-	37000
12-CIT-101*	gas lift	03/07/12 13:05	193	-	39.0	-	196000
12-CIT-102	gas lift	03/07/12 15:55	187	200	49.5	6.6	199000
12-CIT-103*	gas lift	03/07/12 18:05	188	201	45.0	-	198000
12-CIT-104	gas lift	03/07/12 19:50	190	201	41.3	6.4	203000
12-CIT-105	gas lift	03/07/12 21:30	190	201	42.1	6.5	200000
12-CIT-106	ESP	03/14/12 09:20	193	201	29.3	6.5	190000
12-CIT-107	ESP	03/14/12 11:20	191	195	36.6	6.4	189000
12-CIT-108	ESP	03/14/12 13:40	192	198	40.9	6.1	199000
12-CIT-109	VS	03/15/12 11:25	196	199	33.7	5.3	200000
12-CIT-110	VS	03/15/12 17:49	200	-	26.3	5.4	197000
12-CIT-220	gas lift	06/04/12 13:15	187	203	42.4	6.4	201000
12-CIT-221	gas lift	06/04/12 15:30	182	200	49.8	6.4	204000
12-CIT-222	U-tube	06/04/12 19:30	195	202	27.2	6.0	202000
12-CIT-223	VS	06/05/12 11:10	193	201	31.7	5.7	201000
12-CIT-224	U-tube	06/05/12 15:10	186	193	31.7	6.2	185000
12-CIT-225	VS	06/05/12 18:00	197	201	27.3	5.5	201000
13-CIT-103	U-tube	05/20/13 13:00	182	-	30.5	6.1	202000
13-CIT-105	U-tube	05/20/13 18:15	192	-	27.3	6.1	196000

“-“ = not determined

^a All times given are Central Time Zone.

^b Measured conductivities are temperature-corrected to 25 °C by instrument software

^c Not corrected for *in situ* pressure temperature conditions or loss of volatiles. *In situ* T and P were about 106.5°C and 30 MPa.

^d Calculated as the sum of all cation and anion mass, including estimated carbonate species and volatile fatty acids.

* Analyses of these samples was limited to T, conductivity, anions and cations

† Considered estimates because of difficulty in measuring high conductivity (>20 mS/cm) samples

534 Table 3: Results for the determination of cations by ICP-MS.

SAMPLE ID	sampling method	Li mg/L	B mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Fe mg/L	Mn mg/L	Zn mg/L	Cu mg/L	Rb mg/L	Sr mg/L	Ba mg/L	Pb mg/L
12-CIT-100	gas lift	3.1	6	5630	124	9400	2830	28	13	0.97	3.5	1.1	125	4	0.31
12-CIT-101	gas lift	11	47	45090	2220	645	24600	155	56	49	<0.3**	1.8	932	16	4.4
12-CIT-102	gas lift	11	48	45600	2280	647	24900	136	57	50	<0.3**	1.8	947	15	1.1
12-CIT-103	gas lift	11	47	45800	2150	650	25000	118	57	50	<0.2*	1.8	952	17	0.66
12-CIT-104	gas lift	11	46	47000	2200	672	26300	107	57	50	<0.3**	1.8	982	17	0.53
12-CIT-105	gas lift	11	48	45900	2180	648	25500	102	57	51	<0.2*	1.8	974	17	0.35
12-CIT-106	ESP	11	45	44500	2060	676	23900	299	56	56	<0.2*	1.8	921	16	0.29
12-CIT-107	ESP	11	45	44300	1970	667	23500	309	51	51	<0.2*	1.8	907	16	0.19
12-CIT-108	ESP	11	47	46900	2090	646	24900	243	56	54	<0.3**	1.9	957	17	0.61
12-CIT-109	VS	12	48	46800	2200	661	25000	73	57	53	1.8	1.8	959	17	0.54
12-CIT-110	VS	11	47	46300	2100	649	25300	101	57	53	0.79	1.8	962	17	0.52
12-CIT-220	gas lift	11	45	48000	2070	679	25500	116	57	52	<0.2*	1.8	986	17	1.8
12-CIT-221	gas lift	11	48	48400	2150	679	25700	99	58	54	<0.3**	1.9	992	17	0.51
12-CIT-222	U-tube	11	48	47200	2210	713	25200	140	59	55	8.0	1.8	984	17	7.3
12-CIT-223	VS	11	47	48800	2140	690	23500	129	56	53	4.4	1.8	905	17	9.6
12-CIT-224	U-tube	10	40	41800	1730	985	23000	101	44	38	0.26	1.7	882	15	0.77
12-CIT-225	VS	11	47	48000	2110	685	25300	115	56	53	1.7	1.8	990	17	9.0
13-CIT-103	U-tube	9.7	47	47200	2240	882	23800	311	59	54	1.0	1.9	970	10	0.9
13-CIT-105	U-tube	9.5	48	45700	2200	814	23800	271	59	53	0.8	1.9	959	15	1.3

535
536 *less than limit of detection (MDL)
537 **less than limit of quantitation (LOQ)
538 Values in italics are not within the range of lowest to highest calibration standards
539 Results were below detection limit (<MDL) for Al (<0.4), Si (<20), V (<0.2), Cr (<0.6), Mo (<0.4), Cs (<0.4) and U (<0.01)
540
541

542 Table 4: Results for the determination of anions by high performance ion chromatography.

SAMPLE ID	samplin g method	Cl ⁻ mg/L	Br ⁻ mg/L	SO ₄ ²⁻ mg/L
12-CIT-100	gas lift	18700	90	148
12-CIT-101	gas lift	122000	838	313
12-CIT-102	gas lift	123000	861	321
12-CIT-103	gas lift	123000	848	306
12-CIT-104	gas lift	125000	861	319
12-CIT-105	gas lift	123000	858	299
12-CIT-106	ESP	117000	826	316
12-CIT-107	ESP	117000	825	318
12-CIT-108	ESP	122000	859	291
12-CIT-109	VS	123000	832	277
12-CIT-110	VS	121000	811	279
12-CIT-220	gas lift	123000	858	294
12-CIT-221	gas lift	125000	867	301
12-CIT-222	U-tube	124000	856	287
12-CIT-223	VS	124000	828	277
12-CIT-224	U-tube	115000	764	318
12-CIT-225	VS	122000	851	280
13-CIT-103	U-tube	125000	937	311
13-CIT-105	U-tube	121000	859	301

543

544 *less than limit of detection (MDL)

545 For all samples, concentrations of F⁻, NO₃⁻, NO₂⁻, and PO₄³⁻ were below detection limit (<1 mg/L)

546

Table 5: Results for the determination of alkalinity and dissolved sulfide by titration, and ammonia ion selective electrode; dissolved inorganic carbon isotopic composition ($\delta^{13}\text{C-DIC}$) using combustion-interfaced cavity ring-down spectroscopy; and naturally occurring radioactive materials (^{226}Ra) using an ultra-low background high-purity germanium (HPGe) well detector.

SAMPLE ID	sampling method	alkalinity [†] mg/L as HCO_3^-	$\delta^{13}\text{C-DIC}$ (‰)	sulfide mg/L	NH_3 mg/L	^{226}Ra pCi/L
12-CIT-100	gas lift	-	-	-	6	-
12-CIT-101	gas lift	-	-	-	-	-
12-CIT-102	gas lift	180	-10.6	<1*	33	-
12-CIT-103	gas lift	-	-	-	34	-
12-CIT-104	gas lift	140	-13.3	<1*	33	-
12-CIT-105	gas lift	130	-12.2	<1*	33	-
12-CIT-106	ESP	90	-20.2	<1*	32	-
12-CIT-107	ESP	78	-16.9	<1*	33	-
12-CIT-108	ESP	240	-12.4	<1*	33	-
12-CIT-109	VS	150	-17.3	-	33	-
12-CIT-110	VS	180	-17.7	-	-	-
12-CIT-220	gas lift	150	-	<1*	34	-
12-CIT-221	gas lift	150	-11.9	<1*	34	1600±400
12-CIT-222	U-tube	270	-11.6	-	33	-
12-CIT-223	VS	220	-17.5	-	33	-
12-CIT-224	U-tube	170	-16.2	-	32	1700±350
12-CIT-225	VS	190	-17.7	-	33	-
13-CIT-103	U-tube	182	-	-	-	-
13-CIT-105	U-tube	196	-8.4	-	-	-

“-“ = not determined

*less than limit of detection (MDL)

† alkalinity values should be considered as estimates because of the difficulty in measuring pH in high conductivity (>20 mS/cm) samples

558 Table 6: Results for the determination of volatile fatty acids (VFAs) by high performance ion
559 chromatography, and DOC (mg C/L) by high-temperature catalytic oxidation.
560

SAMPLE ID	sampling method	Formate mg/L	Acetate mg/L	Sum VFAs mg C/L	DOC mg C/L
12-CIT-102	gas lift	<0.1*	1.6	0.33	7.5
12-CIT-104	gas lift	<0.1*	1.4	0.28	5.1
12-CIT-105	gas lift	0.3	1.5	0.39	4.7
12-CIT-106	ESP	1.5	2.9	1.0	13
12-CIT-107	ESP	2.0	3.1	1.1	12
12-CIT-108	ESP	<0.1*	1.4	0.29	5.4
12-CIT-109	VS	1.0	1.9	0.63	5.1
12-CIT-110	VS	<0.1*	1.4	0.28	4.0
12-CIT-221	gas lift	<0.1*	1.4	0.28	5.6
12-CIT-222	U-tube	<0.1*	1.0	0.21	2.9
12-CIT-223	VS	<0.1*	1.2	0.25	6.3
12-CIT-224	U-tube	2.0	3.8	1.3	28
12-CIT-225	VS	<0.1*	1.4	0.29	6.9
13-CIT-103	U-tube	-	-	-	-
13-CIT-105	U-tube	<0.1*	<0.5	<0.3	4.5

561

563 *less than limit of detection (MDL)
564 For all samples, concentrations of propionate and butyrate were below detection limit (<0.1 mg/L)

565

Table 7: Gas composition (in percent) for samples collected with downhole vacuum sampler (VS) sampler, U-tube, and at the wellhead in 2012 and 2013.

ID	12-CIT-109	12-CIT-110	12-CIT-224	12-CIT-224-R [‡]	12-CIT-225	12-CIT-G1	12-CIT-G2
Well	D-9-8 #2	D-9-8 #2	D-9-8 #2	D-9-8 #2	D-9-8 #2	D-9-8 #2	D-9-8 #2
Sampler	VS	VS	U-tube	U-tube	VS	Wellhead	Wellhead
Date	3/15/2012	3/15/2012	6/5/2012	6/5/2012	6/5/2012	3/13/2012	3/14/2012
H ₂	1.3	3.1	9.0	10	2.3	0.99	1.1
Ar	0.94	0.68	0.087	0.10	0.56	0.37	0.013
O ₂	1.5	<0.0005	<0.0005	<0.0005	<0.0005	2.8	<0.0005
N ₂	79	71	58	53	64	90	96
CH ₄	15	21	24	29	32	5.1	3.0
CO ₂	2.6	3.9	9.2	7.8	0.74	0.029	0.0076
C ₂ H ₆	0.029	0.046	0.050	0.052	0.082	0.0081	0.0053
CO	0.009	0.006	<0.001	<0.001	0.18	0.44	0.056
C ₃ H ₈	0.0007	0.001	0.002	0.001	0.003	0.0009	<0.0005
C ₂ H ₄	0.0004	0.0006	0.002	0.003	0.001	0.01	0.01

"-" not determined

[‡] Field replicate

For all samples H₂S, C₄H₁₀, and isobutane (iC₄H₁₀) were below the minimum detection limit (<0.0005%).

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References

- Aksoy, N., 2007. Optimization of downhole pump setting depths in liquid-dominated geothermal systems: A case study on the Balcova-Narlıdere field, Turkey. *Geothermics* 36, 436–458.
- Barcelona, M.J., 1990. Uncertainties in Ground Water Chemistry and Sampling Procedures, *In* Chemical Modeling of Aqueous Systems II. American Chemical Society, pp. 310–320.
- Barton, P.B., Chou, I.-M., 1993. Calculation of the vapor-saturated liquidus for the NaCl-CO₂-H₂O system. *Geochim Cosmochim Acta* 57, 2715–2723.
- Bishop, P.K., 1990. Precipitation of dissolved carbonate species from natural waters for $\delta^{13}\text{C}$ analysis—A critical appraisal. *Chemical Geology* 80, 251–259.
- Conaway, C.H., Thomas, R.B., Saad, N., Thordsen, J.J., Kharaka, Y.K., 2015. Carbon isotope analysis of dissolved organic carbon in fresh and saline (NaCl) water via continuous flow cavity ring-down spectroscopy following wet chemical oxidation. *Isotopes in Environmental & Health Studies* 51, 344–358.
- Crozier, T.E., Yamamoto, S., 1974. Solubility of hydrogen in water, seawater, and NaCl solutions. *J. Chem. Eng. Data* 19, 242–244.
- Drummond, S.E., 1981. Boiling and Mixing of Hydrothermal Fluids: Chemical Effects on Mineral Precipitation. Pennsylvania State University, p. 760.
- Eaves, E., 1976. Citronelle Oil Field, Mobile County, Alabama. *American Association of Petroleum Geologists Memoir* 24, 259–275.
- Engle, M.A., Rowan, E.L., 2013. Interpretation of Na-Cl-Br Systematics in Sedimentary Basin Brines: Comparison of Concentration, Element Ratio, and Isometric Log-ratio Approaches. *Math Geosci* 45, 87–101.
- Esposito, R.A., Pashin, J.C., Hills, D.J., Walsh, P.M., 2010. Geologic assessment and injection design for a pilot CO₂-enhanced oil recovery and sequestration demonstration in a heterogeneous oil reservoir: Citronelle Field, Alabama, USA. *Environ. Earth Sci.* 60, 431–444.
- Esposito, R.A., Rhudy, R., Trautz, R.C., Koperna, G.J., Hill, G., 2011. Integrating carbon capture with transportation and storage. *Energy Procedia* 4, 5512–5519.
- Fisher, A.T., Becker, K., 1993. A Guide to ODP Tools for Downhole Measurement, Technical Note No. 10. Ocean Drilling Program, Texas A&M University, p. 131.
- Fisher, R.S., 1998. Geologic and geochemical controls on naturally occurring radioactive materials (NORM) in produced water from oil, gas, and geothermal operations. *Environmental Geosciences* 5, 139–150.
- Freifeld, B.M., Trautz, R.C., Kharaka, Y.K., Phelps, T.J., Myer, L.R., Hovorka, S.D., Collins, D.J., 2005. The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO₂ sequestration experiment. *J Geophys Res-Sol Ea* 110.
- Friedmann, S.J., 2007. Geological carbon dioxide sequestration. *Elements* 3, 179–184.
- Harvey, O.R., Qafoku, N.P., Cantrell, K.J., Lee, G., Amonette, J.E., Brown, C.F., 2013. Geochemical Implications of Gas Leakage associated with Geologic CO₂ Storage-A Qualitative Review. *Environ. Sci. Technol.* 47, 23–36.
- Hitchon, B., Perkins, E.H., Gunter, W.D., 2001. Recovery of trace metals in formation waters using acid gases from natural gas. *Appl. Geochem.* 16, 1481–1497.

IEA, 2013. Technology Roadmap: Carbon Capture and Storage. Organisation for Economic Cooperation and Development/International Energy Agency, Paris.

Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., Freifeld, B.M., 2006a. Gas-water-rock interactions in Frio Formation following CO₂ injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology* 34, 577-580.

Kharaka, Y.K., Cole, D.R., Thordsen, J.J., Gans, K.D., Thomas, R.B., 2013. Geochemical monitoring for potential environmental impacts of geologic sequestration of CO₂ Reviews in Mineralogy and Geochemistry 77, 399-430.

Kharaka, Y.K., Cole, D.R., Thordsen, J.J., Kakouros, E., Nance, H.S., 2006b. Gas-water-rock interactions in sedimentary basins: CO₂ sequestration in the Frio Formation, Texas, USA. *Journal of Geochemical Exploration* 89, 183-186.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., DeBraal, J.D., 1988. SOLMINEQ.88: A Computer Program for Geochemical Modeling of Water-Rock Interactions. US Geological Survey Water Resources Investigation Report, pp. 420.

Kharaka, Y.K., Hanor, J.S., 2014. Deep Fluids in Sedimentary Basins, in: Holland, H.D., Turekian, K.K. (Eds.), *Surface and Groundwater, Weathering and Soils*, 2nd ed. Elsevier Science, Amsterdam, pp. 471-515.

Kharaka, Y.K., Maest, A.S., Carothers, W.W., Law, L.M., Lamothe, P.J., Fries, T.L., 1987. Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A. *Appl. Geochem.* 2, 543-561.

Kharaka, Y.K., Thordsen, J.J., 1992. Stable isotope geochemistry and origin of water in sedimentary basins, in: Clauer, N., Chaudhuri, S. (Eds.), *Isotope Signatures and Sedimentary Records*. Springer-Verlag, Berlin, pp. 411-466.

Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Cole, D.R., Phelps, T.J., Bullen, T.D., 2007. Potential environmental issues of CO₂ storage in saline aquifers: Geochemical results from the Frio Brine pilot tests, Texas, USA. *Geochim Cosmochim Acta* 71, A481-A481.

Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Nance, H.S., Cole, D.R., Phelps, T.J., Knauss, K.G., 2009. Potential environmental issues of CO₂ storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA. *Appl. Geochem.* 24, 1106-1112.

Koperna, G.J., Kuuskraa, V., Riestenberg, D., Rhudy, R., Trautz, R., Hill, G., Esposito, R., 2013. The SECARB Anthropogenic Test: status from the field. *Energy Procedia* 37, 6273-6286.

Kraemer, T.F., Kharaka, Y.K., 1986. Uranium geochemistry in geopressured geothermal aquifers of the United States Gulf Coast. *Geochim Cosmochim Acta* 50, 1233-1238.

Kraemer, T.F., Reid, D.F., 1984. The occurrence and behavior of radium in saline formation water of the U.S. Gulf Coast region. *Isotope Geosciences* 2, 153-174.

Lico, M.S., Kharaka, Y.K., Carothers, W.W., Wright, V.A., 1982. Methods for Collection and Analysis of Geopressurized Geothermal and Oil-Field Waters, US Geological Survey Water Supply Paper.

Lu, J.M., Kharaka, Y.K., Thordsen, J.J., Horita, J., Karamalidis, A., Griffith, C., Hakala, J.A., Ambats, G., Cole, D.R., Phelps, T.J., Manning, M.A., Cook, P.J., Hovorka, S.D., 2012. CO₂-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO₂ sequestration site, Mississippi, U.S.A. *Chemical Geology* 291, 269-277.

MacGowan, D.B., Surdam, R.C., 1990. Importance of organic-inorganic interactions during progressive clastic diagenesis, in: Melchior, D.C., Bassett, R.L. (Eds.), *Chemical*

Modeling of Aqueous Systems II. American Chemical Society Symposium Series, Washington, DC.

Parker, L.V., 1994. The effects of ground water sampling devices on water quality: a literature review. *Ground Water Monitoring & Remediation* 14, 130–141.

Rounds, S.A., 2012. Alkalinity and acid neutralizing capacity (ver. 4.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., sec. 6.6, September 2012, accessed December 22, 2015, from <http://pubs.water.usgs.gov/twri9A6/>.

Schuller, R.M., Gibb, J.P., Griffin, R.A., 1981. Recommended sampling procedures for monitoring wells. *Ground Water Monitoring & Remediation* 1, 42–46.

Stolzenburg, T.R., Nichols, D.G., 1985. Preliminary Results on Chemical Changes in Groundwater Samples due to Sampling Devices. Electric Power Research Institute Report EA-4118, Palo Alto, CA, p. 104.

Stumm, W., Morgan, J.J., 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3rd ed. ed. Wiley, New York :.

Weiss, R.F., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep Sea Res. A* 17, 721–735.

Wolff-Boenisch, D., Evans, K., 2014. Review of available fluid sampling tools and sample recovery techniques for groundwater and unconventional geothermal research as well as carbon storage in deep sedimentary aquifers. *Journal of Hydrology* 513, 68-80.

Figures

Figure 1: Conductivity (mS/cm) versus time, with volume of brine produced during and after initial well circulation using gas lift in March 7, 2012. Collection of first five 12-CIT samples are indicated.

Figure 2: Plot used in initial screen of brine data showing bromide concentration versus the ratio of the concentration (mg/L) of cations Na and K. Methods are gas lift (blue markers), electric submersible pump (ESP, red markers), downhole vacuum sampler (VS, black markers), and U-tube (green markers). Open markers represent March 2012 samples, closed markers are June 2012 samples, and closed-crossed markers are 2013 samples.

Figure 3: Distribution of Cl and Br in brine samples. Data for the local groundwater, and data for the evaporation of seawater (McCaffrey et al., 1987) are also shown. Methods are gas lift (blue markers), electric submersible pump (ESP, red markers), downhole vacuum sampler (VS, black markers), and U-tube (green markers). Open markers represent March 2012 samples, closed markers are June 2012 samples, and closed-crossed markers are 2013 samples.

Figure 4: Plot of pH or carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$) vs alkalinity (as mg/L HCO_3^-) for brine samples. Methods are gas lift (blue markers), electric submersible pump (ESP, red markers), downhole vacuum sampler (VS, black markers), and U-tube (green markers). Open markers represent March 2012 samples, closed markers are June 2012 samples, and closed-crossed markers are 2013 samples.

Figure 5: Ratio of N_2 to Ar (v/v) in gas samples. Methods are downhole vacuum sampler (VS), U-tube, and wellhead sampling.

Figure 6: Concentration of N_2 and CH_4 (volume %) in gas samples. Methods are downhole vacuum sampler (VS, black markers), U-tube (green markers), and wellhead sampling (grey markers). Open markers represent March 2012 samples, and closed markers are June 2012 samples.