Geochemical Impacts of Leaking CO₂ from Subsurface Storage Reservoirs to an Unconfined Oxidizing Carbonate Aquifer

Guohui Wang¹, Nikolla P. Qafoku^{1}, Amanda R. Lawter¹, Mark Bowden², Omar Harvey³, Charlotte Sullivan¹ and Christopher F. Brown¹*

¹Pacific Northwest National Laboratory, Richland, WA 99352

²Environmental Molecular Science Laboratory, PNNL, Richland, WA 99352

³University of Southern Mississippi, Hattiesburg, MS

Submitted to: IJGGC

May 2015

*Corresponding Authors: Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MSIN: P7-54, Richland, WA 99352, Phone: (509) 371-6089, E-mail: nik.qafoku@pnnl.gov

Abstract

A series of batch and column experiments combined with solid phase characterization studies was conducted to evaluate the impacts of the potential leakage of carbon dioxide (CO₂) from deep subsurface storage reservoirs to overlying potable carbonate aquifers. The main objective was to gain an understanding on CO₂ gas-induced changes in aquifer pH and mobilization of major, minor, and trace elements from dissolving minerals in rocks representative of an unconfined, oxidizing carbonate aquifer within the continental US. Samples from the unconfined portion of the Edwards limestone aquifer in Texas were exposed to a CO₂ gas stream or were leached with a CO₂-saturated influent solution simulating different leaking scenarios [i.e., sudden, fast, and short-lived release of CO₂ (batch experiments) and gradual release (column experiments)]. The results from the batch and column experiments confirmed that exposure to excess CO₂ gas caused significant decrease in pH (about two pH units); the release of major chemical elements into the contacting aqueous phase (such as Ca, Mg, Ba, Sr, Si, Na, and K); the mobilization and possible rapid immobilization of minor elements (such as Al and Mn), which are able to form highly reactive secondary phases; and sustained but low-concentration releases of some trace elements (such as Mo, Cs, Sn) in some samples. Spikes of low concentrations of other trace elements (such as As, Cd, Pb, Cu, Zn, Se, etc.), were observed sporadically during these experiments. The results help in developing a systematic understanding of how CO₂ leakage is likely to influence pertinent geochemical processes (such as dissolution/precipitation and sorption/desorption) in the aquifer sediments and will support site selection, risk assessment, policy-making, and public education efforts associated with geologic CO₂ sequestration.

Keywords: CO₂ gas leakage; batch and column experiments; release of major, minor and trace elements

1. Introduction

The capture and storage of carbon dioxide (CO₂) in deep geologic formations (or geologic CO₂ sequestration) is widely considered a feasible option for mitigating anthropogenic CO₂ emissions. However, not all potential risk factors associated with this technology have been carefully identified. For example, a possible risk factor and barrier to widespread deployment of geologic CO₂ sequestration is the potential leakage of CO₂ from the deep storage reservoirs into overlying aquifers, which may have a deleterious impact on groundwater quality. A systematic understanding of how CO₂ leakage would affect the geochemistry of potable aquifers, and subsequently control or affect contaminant mobilization via dissolution, desorption, and/or redox reactions, is required for assessing risk.

Two CO₂ leakage scenarios are possible (Bachu, 2008; Metz et al., 2005). The first is where there is a sudden, fast, and short-lived release of CO₂, as would occur in the case of well failure (Damen et al., 2005; Holloway, 2007; Jordan and Benson, 2009; Skinner, 2003). The second is where the leak is more gradual, occurring along undetected faults, fractures, or well linings (Annunziatellis et al., 2008; Bachu, 2008; Celia and Nordbotten, 2009; Damen et al., 2005; Lewicki et al., 2007; Nordbotten et al., 2005; Scherer et al., 2011). Such diffusive leakage has the greater potential to cause broad-scale environmental impacts due to challenges associated with its detection (Bachu, 2008; Damen et al., 2005; Metz et al., 2005).

Knowledge of the environmental consequences associated with CO₂ leakage is continually evolving (Qafoku et al., 2013; Qafoku et al., 2014). Supercritical CO₂ will undergo exsolution (i.e., phase change from liquid to gas) as it migrates from deep geologic formations to shallower depths in the subsurface. Upon entering an aquifer, a portion of the CO₂ gas will dissolve into groundwater, which will cause a subsequent decrease in aqueous pH of approximately 1 to 3 units due to the formation of carbonic acid (Trautz et al., 2013; Varadharajan et al., 2013). Changes in pH will likely promote the release of major elements (such as Ca, Si, Na, K, Ba, Sr, and Mg), minor elements (such as Fe, Al and

Mn), and trace elements (such as Pb, As and Cd) into the aqueous phase (Little and Jackson, 2010a; Lu et al., 2010; Wang and Jaffe, 2004). The CO₂-induced reactions may therefore lead to the degradation of water quality via mobilization of potential contaminants or changes in other water quality parameters, such as alkalinity (Yang et al., 2014), salinity (Keating et al., 2013b), or total dissolved solids (TDS) (Dai et al., 2014).

Several reviews have been published that describe different aspects of how CO₂ leakage from deep subsurface storage reservoirs would likely affect the geochemistry of overlying potable aquifers (Apps et al., 2010; Harvey et al., 2013). Despite an increase in research and evidence for both beneficial and deleterious consequences of CO₂ migration into potable aquifers and the vadose zone (Harvey et al., 2013), significant knowledge gaps still exist and additional experimental work is needed to document different aspects of the potential implications of CO₂ leakage from deep subsurface storage reservoirs and the effects on the aquifer and groundwater quality.

Although the interest of the scientific community to address scientific issues related to the potential effects of CO₂ leakage from the deep subsurface storage has recently increased (Dafflon et al., 2013; Gilfillan and Haszeldine, 2011; Humez et al., 2013; Keating et al., 2011; Keating et al., 2013a; Kharaka et al., 2010a; Little and Jackson, 2010b; Lu et al., 2010; Navarre-Sitchler et al., 2013; Peter et al., 2012; Smyth et al., 2009; Zheng et al., 2012), many aspects of the CO₂ gas interaction with the aquifer sediments are not well documented in the literature. The degree of perturbation and response to the leaked CO₂ gas induced changes would depend on the aquifer system's specific attributes, the aquifer's physical and mineralogical characteristics (Cahill et al., 2014; Frye et al., 2012), and the rate and extent of chemical, hydrological (Keating et al., 2013b), and biological processes (Harvey et al., 2014) under leak- specific conditions (Wilkin and Digiulio, 2010).

Many of the studies have focused on sandstone aquifers (Cahill and Jakobsen, 2013; Carroll et al., 2009; Dafflon et al., 2013; Keating et al., 2010; Kharaka et al., 2010b; Kirsch et al., 2014; Spangler

et al., 2010; Varadharajan et al., 2013; Zheng et al., 2012). A recent study (Cahill et al., 2013) considered samples with >2% total inorganic carbon to be “carbonate dominated,” and concluded that these samples released greater amounts of trace elements but decreased pH less than silicate dominated samples. Using Cd laden illite, (Frye et al., 2012) determined carbonate content as low as 10% mitigated the effect of CO₂ injection and the desorbed Cd was below detection. However, we are not aware of studies using carbonate aquifer materials, and given their prevalence as sources of potable water overlying potential sequestration reservoirs within the continental United States, there is a need to better understand their response to potential CO₂ gas intrusions.

We conducted a laboratory experimental study with the objective to gain an understanding of how the effects of CO₂ gas are likely to influence: 1) the aqueous phase pH; and 2) mobilization of major, minor, and trace elements from mineral surfaces and bulk structures, in a carbonate aquifer overlying potential deep subsurface CO₂ storage sites. Batch and column experiments combined with solid phase characterization studies (i.e., quantitative X-ray diffraction and acid digestion) were conducted to study the aquifer geochemical changes and to evaluate the potential impacts of the leaking CO₂ from deep subsurface storage reservoirs on aquifer quality. In a companion paper (Bacon et al., 2015), the results from modeling of the experimental data are presented and used to determine mechanisms and refine existing geochemical models, which are then used to predict the water-rock interaction mechanisms under these conditions. Although the effects of water-rock interactions may be site-specific, the results from this experimental research effort combined with the modeling data will help in developing a systematic understanding of how CO₂ leakage is likely to influence pertinent geochemical processes (e.g., dissolution/precipitation and sorption/desorption) for the Edwards aquifer specifically, and for carbonate aquifers in general.

2. Material and Methods

2.1. Samples from the Edwards aquifer, Texas.

A total of six representative rock samples (samples 1- 6) from the Edwards aquifer were used in this study. The Edwards aquifer in Texas is a soluble limestone formation, dominated by karst dissolution features and is representative of carbonate aquifers overlying potential CO₂ sequestration repositories within the continental U.S. The rock samples were collected from outcrops within the unconfined portion of the Edwards aquifer located near San Antonio, Texas. All samples were air dried. The samples 1-3 (i.e., rocks without clay minerals present) were hammer-cracked and ground and sieved. Sample 4 was ground and sieved and samples 5-6 were just sieved. All samples were sieved to pass through a < 2 mm sieve so the same size fraction separated from all these samples was subsequently used in the experiments conducted during this investigation; therefore the data generated from these experiments are comparable. A subset of the <2 mm size fraction was further ground and sieved to separate smaller size-fractions, i.e., <2 mm, 2 mm-53 µm and <53 µm and were used in solid phase characterization studies. The first three samples did not contain clay minerals, while the other samples have clays present in them. The experiments conducted during this investigation tested if the carbonate aquifer materials with or without secondary clay minerals produced greater contaminant mobilization.

2.2. Solid sample characterization: XRD analyses, SEM/EDS measurements and acid extractions

The mineralogy of the collected samples was identified using powder Cu-K α radiation X-ray diffraction (XRD) analyses (Panalytical X'Pert Bragg-Brentano diffractometer) where the mineral signal patterns were collected between 5 and 75° 2 θ with counting for 2s at 0.04° 2 θ steps. All diffractograms produced were analyzed and fitted using the JADE software package (Materials Data Inc., Livermore, CA) for mineral identification.

In addition to XRD analysis, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) were conducted on select samples. SEM and EDS was used to describe calcite morphology and to locate other minerals within the predominantly calcite sediments. Individual clasts of

the <2 mm and <53 μm size fractions were carbon coated to make them electrically conductive and then examined using a JEOL 6340f SEM. Images were collected using a backscattered electron detector.

To determine the amount of major, minor, and trace elements present in the aquifer sediments (i.e., solid-phase chemical composition) that may potentially be released from aquifer materials, a series of concentrated acid digestion was conducted, following ASTM D 5198 (<http://www.astm.org/Standards/D5198.htm>), slightly modified [see (Lawter et al., 2015)]. The digested amounts could set an upper limit (conservative) in terms of maximum expected element release from the sediment samples under highly acidic pH conditions, which is not likely attainable under conventional CO_2 leakage scenarios. Acid digestion (duplicate) were performed using 8 M nitric concentrated acid on <2 mm grounded sediments in a 15 mL centrifuge tube at 95 °C for 2 hours. The extract was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ICP-optical emission spectroscopy (OES) for the soluble elements.

2.3. Synthetic groundwater preparation

A synthetic groundwater (SGW) solution similar in composition to the Edwards aquifer groundwater (GW), based on U.S. Geological Survey data of the Edwards GW aquifer (Musgrove et al., 2010), was used in the batch and column studies. Table 1 (Musgrove et al., 2010) shows the chemical composition of the synthesized GW, as well as the USGS Edwards aquifer analysis. For the SGW preparation, all chemical components were dissolved into laboratory grade distilled water in a polyethylene bottle, while the calcium carbonate was first dissolved in 5 mL of 2% nitric acid, and then added to the solution in order to avoid any precipitation occurring (Table S3). The synthetic groundwater was pH adjusted using KOH and HNO_3 over several days to obtain a stable pH close to 6.9 (representative of the Edwards aquifer GW).

2.4. Batch experiments

Two experimental methodologies were used as part of this research effort: batch experiments to

simulate sudden, fast and short-lived release of CO₂, as might occur in the case of well failure during injection, and column experiments to simulate more gradual leaks through the confining zones, such as those occurring along undetected faults, fractures, or well linings. Both the batch and column experiments were conducted at room temperature (~22 °C) to assess the effects of the leaking CO₂ gas on mineral dissolution/precipitation and/or sorption/desorption reactions in the natural solid materials in near surface aquifers at ambient temperature and pressure conditions.

The batch experimental system used Edwards aquifer materials (system setup apparatus is presented in S1). The < 2 mm size-fraction of the solid materials (5 g) was mixed with the SGW (15 mL) and was exposed to a CO₂ gas stream. The CO₂ gas (99.9% purity) was injected continuously into batch reactors that were open to the atmosphere through a vent to balance the pressure inside the batch reactor. The CO₂ gas intrusion rate was about 70 mL/min and was monitored frequently using a flow meter. Although these rates were lower than the flow rates used by Little and Jackson, 2010 (i.e., 200 mL/min), the CO₂ gas injection rates applied in these experiments were still high enough to ensure that the aqueous phase in the batch reactors was saturated with CO₂ at all times. This is important because if the CO₂ is not in excess, the pH will be buffered by calcite or other dissolving minerals, and the extent and rate of reactions that control contaminant release will change as well.

Through this batch setup, six short-term experiments (called “Experiment 1 – 6”, see section 1 in the Supplementary Data File) were conducted, one per each corresponding material (sample 1 – 6), respectively. The experiments lasted for 4, 8, 12 and 24 hours and 2, 3, 7 and 14 days. Each experiment (e.g., the ones at 4 hours, 8 hours, etc.) was run in two replicates and a blank. At the end of the experimental time, the supernatant was filtered through a 0.22-µm filter for elemental analysis by ICP-MS and ICP-OES. A subsample of the liquid phase in the reactors was collected immediately after the elapsed time for pH measurement. In addition, one long-term experiment using sample 2 was conducted for 119 days. Other details pertaining to the batch experiments are included in the

2.5. Column Experiments

In this study, we used column experiments to investigate major, minor, and trace element release from the crushed rocks when they are exposed to CO₂ gas-saturated SGW. Figure 1 shows the schematic of the column experiment setup, and pictures of the apparatus used in the experiments are presented in Fig. S2. Details about column packing procedure and data interpretation, especially regarding stop flow events, are given elsewhere (Qafoku et al., 2010). The saturation of the synthesized SGW with CO₂ was obtained through continuously injecting 99.9% CO₂ gas into the SGW reservoir (SGW in a 2L polyethylene bottle) at a flow rate of about 0.52 mL/min, where the CO₂ gas flow was driven by a gas pressure difference of about 3.5 psi (the inlet pressure was adjusted to 4 psi through the CO₂ gas cylinder valve, and a single direction release valve with a gas release pressure of 0.5 psi was installed in the reservoir as a vent). The 2 L SGW was saturated for one day before injection into the reaction column, and the CO₂ stream was continuously injected into the SGW reservoir throughout the experiment. Our pH-kinetic experiments showed that the pH of the reservoir SGW was quite stable (~ pH 4.1) after the initial ~ 30 h CO₂ gas purging with the CO₂ gas flow rate of ~ 0.52 mL/min in both 2 and 4 L synthesized groundwater solutions (see Figure S7 in Supplementary Information File). All experiments were conducted under hydraulically saturated condition. The CO₂ saturated SGW was injected continuously into the columns from the bottom inlet using a KLOEHN V6 syringe pump at a relatively slow flow rate of about 0.03 mL/min (HPLC pumps were used in the initial ~50 hours for the first set of columns). Changes in effluent pH and Eh were measured online with high resolutions (hourly for pH), and the effluents were collected for chemical concentration analysis using ICP-MS and ICP-OES. For each column experiment, the stop-flow (SF) technique was applied (one or two times) to assess the effect of time-dependent reactions and processes on chemical element release. The fluid residence time was increased during SF to probe the system's buffering capacity (i.e., measure pH increase during the SF events) and changes in chemical composition. Selected column parameters are

presented in Table 2. Four samples (Sample 1, 3, 4, and 5) were used in the column experiments. In addition, a control column was packed with Accusand and was leached under conditions similar to those containing the crushed Edwards aquifer rock.

The column studies were split into three sets with two columns conducted in each set. For the experiments of Set 1, the materials were dry-packed into a glass column with an inner diameter (ID) of 2.49 cm and length of 15.2 cm: a 0.45 μm Millipore filter was used at both ends of each column to hold the packed materials in place and to filter the effluent solutions. The column 1 of Set1 (hereafter called Accusand) was packed with Accusand. Column 2 was packed with Accusand (2.5 cm length of the top of the column), followed by sample 1 (7.8 cm in length in the middle of the column), and again Accusand (the last 5 cm of the column). Both columns were run in parallel and the Accusand column served as the control. Based on the mass of the packed material and density (2.65 and 2.71 g/cm^3 for Accusand and sample 1, respectively), the estimated porosity for the packed Accusand column was 0.17, and in column 2 (the portion packed with sample 1) was 0.27. After leaching with CO_2 saturated SGW began, the stop flow condition was applied once in set 1 at approximately $t = 320$ hours for a duration of 146 hours.

Set 2 of the experiments used smaller PEEK columns (ID 2.4 cm with column length of 5.7 cm) that were packed with the dry-sieved, <2 mm size fraction Edwards aquifer samples (i.e., samples 1 and 3; porosity 0.25 and 0.27, respectively). The columns were leached with the SGW for about 30 hours and then the input solution was switched to the CO_2 gas saturated SGW. Two stop flow events with durations of 143 and 69 hours were applied during leaching with the CO_2 gas saturated SGW at approximately 170 and 240 hours of experimental time, respectively. The column solution residence time during flow through was 4.5 hours for sample 1 and 3.9 hours for sample 3. Set 3 experiments used identical columns to those used in Set 2. The columns were packed with the dry-sieved, <2 mm size fraction Edwards aquifer (samples 4 and 5; porosity was 0.26 and 0.36, respectively). The columns

were leached with SGW for about 110 hours and then the input solution was switched to the CO₂ gas saturated SGW. Two stop flow events of 118 and 195 hour durations were applied during leaching with the CO₂ saturated SGW. The column solution residence time during flow was 3.8 and 5.1 hours for samples 4 and 5, respectively. Additional information about the column experiments is provided in section 3 of the Supplementary Information File.

3. Results

3.1. Solid sample characterization: XRD, SEM/EDS and acid extractions

The XRD results showed that calcite was the predominant mineral phase in most of the samples (Table 3). Clearly, these analyses showed that the mineralogy of samples 1-3 was exclusively dominated by calcite (~100% based on XRD). The other three samples (samples 4-6) contained clays and secondary minerals in addition to calcite, and represented clay containing rocks mixed with soil particles formed as a result of diagenesis and pedogenesis. Samples 4-6 had appreciable amounts of quartz, and montmorillonite. Karst allows these materials to infiltrate fractures and voids within the solid rock. Montmorillonite, which apparently has variable interlayer spacing because of the presence of interlayer water content and cations, was more difficult to quantify than expected. None of the crystal structures in the database or literature gave an adequate fit to the clay peaks present in this sample set, although the peaks had a good match to several of the montmorillonite patterns in the International Centre for Diffraction Data (ICDD) database.

SEM micrographs and EDS chemical analysis measurements were used to describe the morphology of calcite and to locate other minerals determined by XRD. For example, calcite, quartz, and phyllosilicates were all present in sample 4 (Fig. S11). The rough surfaces of calcite explain the fast rate of dissolution observed in batch experiments (data presented below). Phyllosilicates were also located in other clay containing samples (in one location, a 2:1 concentration ratio for Al and Si was found, which is a typical combination for montmorillonite, Fig. S11c). In additional EDS

measurements, the underlying grain where phyllosilicate particle was found was determined to be calcite. SEM and EDS results for sample 2 (which is a representative of the rock samples without clays) showed only calcite (different morphologies of calcite are presented in Fig. S12).

The results from the 8-M acid digestion of the samples clearly show that the solid materials have significant amounts of trace elements and potential contaminants, such as As, Cd, Cr, Pb, and, in some samples, Zn. Table S7 includes the concentrations of several elements extracted from the solid samples (additional data are included in Tables S1 and S2). Although the conditions of the acid digestion were extreme in terms of pH and temperature (i.e., 90 °C), the results confirmed that the Edwards aquifer samples contained trace metals, which may or may not be released when sediments are exposed to the CO₂ gas.

3.2. Batch experiments

The initial and continued pH measured in the blanks varied between 7.5 and 8 in all experiments and remained in this range or decreased slightly (average pH of the blanks was 7.33 – 7.80) (Fig. 2). However, the pH of the CO₂ gas-treated samples decreased significantly and varied between 6.03 to 6.16 in the different experiments. The decrease in pH was a result of the formation of carbonic acid following the reaction:

The pH of the SGW purged with the CO₂ gas was pH = 4.1 (Fig. S7). Clearly, the aqueous phase pH was buffered, most likely via calcite dissolution following the reaction:

As a result of pH decrease, the aqueous concentrations of different elements increased significantly and followed similar time-dependent trends to that of pH. For example, compared to concentrations in the blanks, the Ca concentrations increased by 283% (increased from 119.2 mg/L to

456.0 mg/L) and 164% (increased from 223.8 mg/L to 588.9 mg/L) in the experiments conducted with sample 1 and 6, respectively (Fig. 3). In addition, Si concentrations increased significantly by 91-164% in the experiments conducted with samples 4, 5 and 6 after CO₂ gas exposure (Fig. 4). Most likely, Si was released from quartz and montmorillonite present in these samples (Table 3). In contrast, the aqueous Si concentration was below the instrument detection limit (130 µg/L) in the experiments conducted with samples 1, 2 and 3, with calcite as the only detectable mineral.

The concentration of other divalent cations such as Ba, Mg (Fig. S3) and Sr (Fig. S4) also increased significantly in the CO₂-treated experiments. For example, Ba concentrations increased 100% in the experiments conducted with samples 1-3, and more than 330% in the experiment conducted with sample 6. Samples 4-6 released more Ba than samples 1-3 suggesting that reactions other than calcite dissolution may contribute to Ba aqueous concentrations. The concentrations of monovalent cations such as Na and K changed little in the CO₂-treated samples vs. blanks in all experiments. However, consistently greater concentrations were found in the CO₂-treated experiments than in the blanks (e.g., experiments conducted with samples 5 and 6 for K and sample 5 for Na) indicating that the release of these elements in the aqueous phase may be solid sample specific.

Detectable concentrations of minor or trace elements were occasionally measured in these experiments (Table 4). Aqueous Mn concentrations were significantly greater in the CO₂-treated samples in the experiments conducted with samples 4 and 5 (Fig. S5). Except for S and Sn, most elements were undetectable in experiments, either in the presence or absence of the CO₂ gas (except for sample 4, where several elements such as Cu, Mn, Mo, and Cs, were present in the aqueous phase in the CO₂-treated experiments). Detectable concentrations of S (about 6-8 mg/L) were measured in experiments conducted with samples 1, 2 and 4, and the CO₂-exposed samples had consistently greater concentrations than the corresponding blanks. Similar aqueous phase concentrations of S in the CO₂-exposed samples and the blanks were observed in experiments with sample 3, implying that the release

of this element is sample specific. A substantial amount of Sn was released in the aqueous phase of the CO₂-treated samples 1-3 and 6 (sample 3 released the greatest amount).

The long term effect of continuous CO₂ gas exposure was studied for 119 days in experiment 7, conducted with sample 2 (essentially, an extension of experiment 2). The pH values in the CO₂-treated experiments remained unchanged during the entire experiment (the average pH was 6.13, Fig. S6), while a stable value of 7.27 was measured in the blank experiment. The pH was similar to the average pH measured in experiment 2 which lasted for only 14 days. Similarly, the average Ca concentration did not change significantly and remained at 488 mg/L for the duration of this long-term experiment. The constant pH and Ca concentrations measured during this relatively long batch experiment showed that calcite dissolution was fast and reached equilibrium within hours or few days controlling the pH and Ca aqueous concentration.

Decreasing trends of Ba, Mg (data not presented) and Sr concentration were observed with time. The decrease in Ba, and especially Sr, concentration with time was more rapid than that of Mg, indicating different sources or mechanisms of release, and that calcite dissolution was not the only reaction controlling their aqueous concentrations [the mechanisms and important reactions are further explored and discussed in the paper by Bacon et al. (2015)].

Similar trends were observed for other elements. For example, the average Sn concentration decreased from a concentration of about 1300 µg/L measured in 7 days, to about 1000 µg/L in 14, 21, and 28 days, and continued to decrease to about 680 µg/L by 35 and 42 days; Sn was not detected in the aqueous phase after 42 days. Detectable concentrations of Cu (ranging from 11 to 17 µg/L) were measured occasionally in the time interval of 64 to 92 days. The S concentrations changed within a narrow range of 7 and 8 mg/L during the entire experiment. Finally, low and similar Si concentrations, which decreased with time, were observed in both blanks and the CO₂-treated experiments.

3. 3. Column experiments

3.3.1 Set 1: Accusand and sample 1

The first column was packed with pure Accusand and the second column was packed half with Accusand and half with sample 1. Both columns were leached initially with the N₂ gas-saturated SGW followed by the CO₂ gas-saturated SGW. The pH and Eh of the columns' effluent followed a similar decreasing pH and increasing Eh trend when the N₂ gas-saturated SGW was leached through the columns of Accusand and Accusand plus sample 1 (Fig. 5, pH and Eh plots). When the inlet solution was switched to the CO₂ gas-saturated SGW, the pH of the effluent of the Accusand column decreased significantly to about 5, while the pH of the effluent of the column that was partially packed with sample 1 decreased to a pH of about 6.5. In the column packed with sample 1, the pH increased to about 7 during the SF event of 146 hours, but it decreased as soon as flow was reestablished. Clearly, the Edwards aquifer material (sample 1) manifested a greater buffering capacity than the Accusand. In addition, the Edwards aquifer material was able to buffer the aqueous phase pH to values well above (approximately 2.5 pH units) the CO₂ laden SGW influent pH (which was about 4). Another important observation is that the Eh values in both columns increased with leaching time, suggesting increasingly oxidizing conditions in the columns.

In the experiment conducted with sample 1, Ca concentrations increased significantly as soon as the CO₂ gas-saturated SGW was used as the leaching solution (as expected, Ca concentrations did not change in the Accusand column's effluent, Fig. 5). The Ca concentrations decreased during the 146-hour SF event, most likely in response to increasing pH, and then continued the increasing trend as soon as the flow restarted. Steady state Ca concentrations (usually indicative of pseudo equilibrium conditions) were not observed during this experiment indicating that calcite dissolution was slow and time was required to reach equilibrium.

The changes in Si concentration with time were similar in both columns (Fig. 5, Si plot).

Assuming the main Si source was the Accusand, an increase of Si concentration was not expected in the column effluent since quartz solubility is almost constant below pH = 9. Other observations were: As, Al, Mn, Sn, Zn, P, Ni, Se, and Cd concentrations (Fig. S8) were below their estimated quantification limits (EQLs); Cu, Cs, Si, Sr, S, Cr, Mo, Pb concentrations were above detection limits only during leaching with the N₂ gas-saturated SGW and/or during the SF events; Na, Ba, Mg, K concentrations were above detection limits in the effluents of the column packed partially with sample 1; other elements (such as Cs) had effluent concentrations above detection limits that followed similar trends in both columns.

Important potential contaminants, such as Pb, Cs, Cu, and Mo, were detected in the aqueous phase only during the time the columns were leached with the N₂-saturated SGW, thereby confirming that these releases were not a consequence of CO₂ gas exposure to the Edwards aquifer material. Another important observation is that some of the potential contaminants were released into the aqueous phase during the SF events, indicating that the reaction controlling their release was either time-dependent (the fluid residence time increased during the SF events), or pH-dependent because an increase in liquid phase pH was also observed during the SF events.

3.3.2 Set 2: samples 1 and 3

The additional columns were conditioned through SGW flowing for about 30 hours, followed by injection of the CO₂ gas-saturated SGW (Fig. 6). The effluent pH quickly decreased (within the first 10 hours) after injection of the CO₂ gas-saturated SGW and then stabilized to about 6.5 and 6.4 in the experiments conducted with samples 1 and 3 (with a mineralogy predominated by calcite), respectively. The pH measured in the batch experiments conducted with the same sediments (experiment 1 and 3) were lower (6.10 and 6.09, respectively), suggesting that the lower solid-to-solution ratio in batch tests allowed the dissolved CO₂ gas to overpower more of the Edwards aquifer materials' buffering capacity.

Calcium concentrations increased immediately after injection of the CO₂ gas-saturated SGW and

continued to increase for the duration of the experiment without establishing steady-state concentrations (a maximum concentration of about 250 mg/L was reached at the end of this experiment, Fig. 6). The increasing trend, however, was not smooth, indicating that more than one reaction than calcite dissolution (i.e., adsorption, re-precipitation) was affecting and/or controlling the aqueous Ca concentration as the liquid phase moved through the packed column.

Ca concentrations were significantly perturbed in both columns during the two SF events of 143 and 69 hours (pH changed as well during these events), reinforcing the idea that multiple reactions, which might have been time-dependent and/or pH-dependent reactions, were controlling Ca concentrations in the column's liquid phase. The Ca concentrations measured in the batch experiments conducted with the same materials (samples 1 and 3) reached equilibrium fast within the first hours of the experiment, with apparent equilibrium concentrations of 456 and 528 mg/L. However, one should realize that the batch and column systems are fundamentally different in terms of solid-to-solution ratio, removal of reaction products and the fluid residence time, which was much shorter in the column experiments where CO₂ gas-saturated SGW was continuously injected into the columns.

The concentrations of potential contaminants, such as As and Pb (Fig. 6) were mostly below detection limits and increased only during the SF events, when the fluid residence time inside the column and aqueous phase pH increased as well, implying either a flow-rate (time) dependent, non-equilibrium condition or a pH dependent desorption reaction. Other observations were (Fig. S9 and Table 5): Al, Ni and Zr concentrations were below the EQL but were detectable by the equipment used to run the analyses; Cu, Mo, Se, and Ag concentrations were above the EQL only during leaching with SGW and during the SF events; Sb, Ba, Mg, Cs, Si, Na, Sr, and S concentrations (in addition to Ca) were above detection limits in both columns (K was also present but its concentration was affected by the online pH electrode of the column apparatus and for this reason, was not reported).

These results were consistent with the results from the batch experiments presented in

experiments 1 and 3, which used the same solid materials (samples 1 and 3), with some exceptions. The column effluent concentrations of Si and Cs were close to the detection limit and they were not detected consistently in the batch experiments (e.g., Si was detected only in the 2-, 3-, and 7-day samples collected from experiment 3). In addition, Sb was not detected in the batch experiments and Sn was not detected in the column experiments. The concentrations of Cu, Mo, Se, and Ag were apparently controlled by pH-dependent reactions because they were detected only during leaching with the CO₂-free SGW and during the SF events, when a rebound in the aqueous phase pH was observed. Cu and Mo were also detected in the contacting aqueous phase in a few of the batch tests.

3.3.3. Set 3: samples 4 and 5

Effluent pH increased significantly in the experiment conducted with sample 4 and slightly in the other one conducted with sample 5 during column conditioning with the SGW (the first 110 hours) (Fig. 7). The effluent pH decreased fast after injection of the CO₂ gas-saturated SGW (within the first 10 hours) and then stabilized to about 6.2 and 6.3 in samples 4 and 5 (with a more complex mineralogy than samples 1-3). The pH measured in the batch experiments conducted with the same sediments (experiments 4 and 5) was lower (6.10 and 6.03, respectively).

Similar trends to the ones observed in previous experiments were observed in the experiments conducted with samples 4 and 5 in terms of effluent Ca concentration. The increasing trend after CO₂ gas-saturated SGW injection was irregular, indicating multiple reactions control aqueous Ca concentrations. In addition, the Ca concentrations decreased significantly in response to increases in pH during the 118- and 195-hour SF events, reaching low concentrations well below the pseudo steady-state concentrations established in both columns at the beginning of the experiments during leaching with the SGW.

The Si concentration followed two well-distinguished trends in the two sample columns. In sample 4, Si concentrations decreased nonlinearly from about 7 to 1 mg/L in the first 110 hours of the

experiment when the SGW was used to leach the columns; afterwards, it reached a peak maximum concentration of about 9 mg/L immediately after the CO₂ gas-saturated SGW was injected into the column and the relatively short SF event, but then decreased again to values close to the detection limit. Finally, it peaked again during the 118- and 195-hour SF events, but the peak concentrations decreased even though the SF duration increased. This behavior is consistent with the fact that the solid source that was controlling and contributing to the Si concentration in solution was limited in mass. This solid source was most likely distributed throughout the sample matrix because the effluent concentration was a function of the fluid residence time; i.e., it increased during the SF events, indicating that additional time was needed for contributions of the remote sites within the sample matrix to travel through the diffusive pores to the advective pores within the column. The results from this column experiment were also consistent with the results of batch experiment 4 (conducted with the same material), which showed that the Si accumulated in the aqueous phase during 14 days was barely greater than 6 mg/L.

In sample 5, the Si concentration decreased only slightly and established a pseudo steady-state concentration during the first 110 hours of leaching with the SGW (Fig. 7); the effluent pH changed insignificantly during this period of time. However, the effluent Si concentration increased to a new pseudo steady state of about 11.5 mg/L as soon as the CO₂ gas-saturated SGW was injected into the column. The Si concentration decreased significantly during the 118- and 195-hour SF events, most likely in response to changes in pH during the SFs. Most likely, a dissolving Si-bearing phase (silicate or phyllosilicate) was controlling the aqueous Si concentration. This phase (or phases) was able to release Si continuously into the aqueous phase (the influent fluid was Si-free), and sustain relatively constant Si effluent concentrations for the duration of the experiment (about 500 hours). The results from this column experiment are also consistent with the results of batch experiment 5 (conducted with the same material), which showed that the Si concentration reached an apparent equilibrium at a concentration of about 18 mg/L.

Other observations were: Pb concentrations were above detection limit only during leaching with the SGW and during the SF events (Fig. 7, Pb plot); Mo concentrations were above detection limit in the column experiments conducted with sample 4 (Fig. 7, Mo plot); Ba exhibited similar behavior to that of Si during these column experiments (Fig. S10); Al, Bi, Cd, Li, P, U, Ni, and Zr concentrations were below the EQL but were detectable by the equipment used to run the analyses (Fig. S10 and Table 5); As, Cr, Cu, Pb, Mn, Se, and Zn concentrations were above the EQL only during leaching with SGW and during the SF events; Sb, Ba, Mg, Si, Ag, Na, Sr, Sn, and S in addition to Ca concentrations were above detection limits in both columns; relatively low Cs and Mo concentrations (0.5 µg/L and 11 µg/L, respectively) were released from sample 4; Hg concentrations (maximum 30 µg/L) were released from sample 5.

Again, the results from these column experiments are consistent with the results of the batch experiments. For example, the following elements were detected in batch experiments conducted with samples 4 and 5: Si, Ba, Mg, Sr, and Na in addition to Ca. Sulfur and Sn were occasionally detected. Sb and Ag were not detected in the batch experiments and Mn was detected in the column experiments only during leaching with the SGW (the first 110 hours). The concentration of other elements and potential contaminants in column effluents such as As, Cr, Cu, Pb, Mn, Se, and Zn, were mobilized only during leaching with SGW or during the SF events when a rebound in the aqueous phase pH was observed. These intermittent detections most likely were controlled by pH-dependent reactions. Low concentrations of Cr, Cd, and Cu were detected inconsistently, i.e., only at a few time points within batch experiments 4 and 5.

4. Discussion

Results from the short- and long-term batch experiments and those from the column experiments conducted with six representative samples from the Edwards aquifer clearly showed that pH decreased by about one to two units immediately after CO₂ injection and that Ca, Si, Ba, Sr, Mg, Na, K, S, Sb, Ag, Sn and Mn were mobilized and released into the aqueous phase. Calcite dissolution and a series of

exchange and precipitation reactions triggered by calcite dissolution have a crucial role in controlling the aqueous concentration of these elements. Although we are not aware of other studies conducted with carbonate aquifer materials, results from published articles focused on different aquifer types have shown a decrease in pore water pH accompanied by increases in concentrations of some chemical elements such as Ba, Ca, Co, Fe, Mg, Mn, Ni, Sr and others in laboratory batch studies (Little and Jackson, 2010b; Lu et al., 2010; Smyth et al., 2009). In addition, the results from field experiments also showed release of elements into the aqueous phase due to CO₂ injection. For example, a rapid and systematic change in pH, alkalinity, and electrical conductivity, along with an increase in the concentrations of metals such as Ca, Mg, Fe, Mn, and organics (benzene, toluene, ethylbenzene, and xylenes) were observed by Kharaka et al. (2010), although these concentrations were below the U.S. Environmental Protection Agency's maximum contaminant levels (MCL)s. In another controlled-release field experiment conducted in Mississippi (Trautz et al., 2013), a sustained and easily detected pH decrease of about 3 units was observed. Importantly, these authors observed a pulse response for some constituents (e.g., Ba, Ca, Cr, Sr, Mg, Mn, and Fe), which suggested a fast-release mechanism (desorption, exchange, and/or fast dissolution of small finite amounts of metal bearing solids or coatings). Therefore, the results from our study were similar to the results from other studies in terms of pH changes and the release of major elements into the aqueous phase.

Contrary to the results of some studies presented above, our results showed that only low concentrations of minor (Fe and Al) elements were occasionally detected in the aqueous phase. However, this does not mean that these elements were not released from potential Fe and Al bearing phases when these materials were exposed to the CO₂ gas. Usually, it is difficult to detect aqueous Fe concentrations under oxidizing conditions because Fe(III) is removed quickly from solution as a result of precipitation reactions and formation of a variety of Fe oxides and oxyhydroxides. In addition, the solubility of Fe(III) bearing phases is low under conditions relevant to these experiments. Changes in the Fe and Al mineralogy (i.e., dissolution of Fe and Al bearing phyllosilicates and subsequent

formation of other phases) may have occurred during these experiments. However, the importance of these transformations in controlling and/or affecting the fate of different elements released during these experiments was not determined during this investigation.

Potential contaminants, such as As, Cr, Cu, Pb, Mo, Cs, Cr, Cd, Se, and Zn, were only occasionally released into the aqueous phase during these experiments. Some elements (Pb is a good example) were released during leaching with SGW, in the absence of CO₂, and/or during the SF events, indicating that the reaction controlling their release was likely time- and/or pH-dependent, because an increase in liquid-phase pH was also observed during the SF events.

Other studies conducted with materials from carbonate aquifers are not available in the literature and, therefore, a comparison was not possible. In addition, results from studies published in the literature conducted with solid samples from different aquifer types are not conclusive in terms of determining whether there are or are not CO₂-induced deleterious effects on the GW quality (in terms of potential contaminant release). However, lately the predominant thinking is shifting towards no or little negative effects, and that these effects may be site specific. For example, results from field experiments showed that there is no significant degradation of the overlying aquifer GW quality in terms of the drinking water standard due to CO₂ injection (Kharaka et al., 2010a; Trautz et al., 2013), although degradation of the aquifer determined by historical maximum concentrations in the aquifer is also important to consider, as discussed in the accompanying modeling paper (Bacon et al., 2015). Caritat et al. (2013) monitored the GW flow and chemical composition in two overlying aquifers (a shallow, unconfined limestone aquifer and a deeper, confined sandstone aquifer) before, during, and after CO₂ injection into a deep depleted natural gas reservoir and they observed no statistically significant changes of the aquifer property due to the CO₂ injection, although it is important to note that this may have been due to no leakage. Frye et al. (2012) used column experiments packed with Cd-spiked illite mixed with quartz to quantify Cd desorption under varied CO₂ leakage conditions. They found that fast leakage

rates were responsible for earlier and larger amounts of Cd desorption. They suggested that calcite content as low as 10% can mitigate the effect of pH reduction and may result in zero Cd desorption (the calcite dissolution increased the solution pH values preventing Cd desorption). Finally, Montes-Hernandez et al. (2013) demonstrated that remobilization of trace elements by CO₂ intrusion is not a universal physicochemical effect. They found that goethite and calcite, two minerals frequently found in aquifers, could successfully prevent the remobilization of adsorbed Cu, Cd, Se, and As when CO₂ is intruded into the system. In another field study followed by modeling, Apps et al. (2011) concluded sorption/desorption reactions are the likely cause for the quick release of As and Pb, but also found the concentrations were below or close to the respective MCLs. Clearly, the results included in recent publications and those from this study have suggested that the environmental consequences associated with CO₂ leakage from deep subsurface storage reservoirs might be strictly site-specific. Additional work is needed to determine the source(s) of potential contaminants and the mechanisms involved in the mobilization and immobilization reactions.

In our study, we also observed differences in results obtained from batch and column experiments conducted during this investigation. For example, the results from batch and column experiments conducted with the same materials showed differences in pH and the trends of Ca concentration changes as a function of time. In addition, differences were also observed in the concentrations of other elements and potential contaminants between the two test protocols. Gilfillan and Haszeldine (2011) have questioned the results from batch experiments because of high surface areas and over-estimation of the amount of metals released. Because the column system approximates more closely field conditions and results obtained from column experiments are not reported in the current literature, we recommend that the column experimental system should be used more frequently in future experimental efforts within this area of research. This is necessary for a more accurate risk assessment.

5. Conclusions

We conducted a series of batch and column experiments combined with solid phase characterization studies (i.e., quantitative x-ray diffraction and acid digestion) with the objective to evaluate the impacts of the potential leakage of carbon dioxide (CO₂) from deep subsurface storage reservoirs to overlying potable carbonate aquifers. Rocks predominated with calcite, with or without clay minerals, from the unconfined portion of the Edwards limestone aquifer in Texas, which is a representative unconfined, oxidizing carbonate aquifer, were used in this study. The XRD results confirmed that calcite was the only detected phase in some samples. Other samples had a mixture of calcite, quartz and montmorillonite.

The results from the batch and column experiments confirmed significant decreases in aqueous phase pH occur rapidly upon leakage of CO₂ into the aquifer. However, the Edwards aquifer limestone material is able to buffer the aqueous phase pH via calcite dissolution to values well above (approximately 2 to 2.5 pH units) the CO₂-laden influent solution pH (which is about 4). The results also confirmed the release of major chemical elements into the contacting aqueous phase (such as Ca, Mg, Ba, Sr, Si, Na, and K); the mobilization and possible rapid immobilization of minor elements (such as Al, Mn, and in few cases, Fe, which are able to form highly reactive secondary phases); and sustained but low-concentration releases of some trace elements (such as Mo, Cs, Sn) in some samples. Spikes of low concentrations of other trace elements (such as As, Cd, Pb, Cu, Zn, Se, Mo, etc.), were observed sporadically during these experiments. Importantly, the overall results from the batch and column experiments conducted with crushed and/or sieved materials, which are more likely to undergo dissolution because of the higher reactive surface area and, subsequently, release greater amounts of contaminants into the surrounding GW than the rocks, confirmed that the potential contaminants were only occasionally released into the aqueous phase, their concentrations were low and the reactions controlling their release may be pH dependent and site specific.

A detailed discussion of the processes, reactions and mechanisms involved in oxidizing

carbonate aquifers is included in the companion paper by Bacon et al. (2015), where the results from modeling of the experimental data included in this paper are presented. Overall, the results presented in both these papers will help in developing a systematic understanding of how CO₂ leakage is likely to influence pertinent geochemical processes (such as dissolution/precipitation and sorption/desorption) in carbonate aquifer sediments and will support site selection and risk assessment associated with geologic CO₂ sequestration.

Acknowledgments

The U.S. Department of Energy's (DOE's) Office of Fossil Energy has established the National Risk Assessment Partnership (NRAP) Project to better understand and predict risk at CO₂ sequestration sites. The research presented in this paper was completed as part of the GW protection task of the NRAP Project. NRAP funding was provided to PNNL under DOE contract number DE-AC05-76RL01830. The research presented in this paper was conducted in part in the Environmental Molecular Sciences Laboratory, which is a national scientific user facility located at PNNL and operated by Battelle Memorial Institute on behalf of the U.S. DOE OBER. SEM and EDS measurements were taken by Isaac Carrol and we are grateful for his efforts.

Supplementary data

A detailed description of the batch and column experiment methodology and additional experimental data included in tables and figures are presented in the Supplementary Information File.

References

- Annunziatellis, A. et al., 2008. Gas migration along fault systems and through the vadose zone in the Lateral caldera (central Italy): Implications for CO₂ geological storage. *Int. J. Greenhouse Gas Control*, 2(3): 353-372.
- Apps, J.A., Zheng, L., Zhang, Y., Xu, T., Birkholzer, J.T., 2010. Evaluation of Potential Changes in Groundwater Quality in Response to CO₂ Leakage from Deep Geologic Storage. *Transport in Porous Media*, 82(1): 215-246.
- Apps, J.A. et al., 2011. TRANSIENT CHANGES IN SHALLOW GROUNDWATER CHEMISTRY DURING THE MSU ZERT CO₂ INJECTION EXPERIMENT. 10th International Conference on Greenhouse Gas Control Technologies, 4: 3231-3238.
- Bachu, S., 2008. CO₂ storage in geological media: Role, means, status and barriers to deployment. *Prog. Energy Combust. Sci.*, 34(2): 254-273.
- Bacon, D., Qafoku, N.P., Dai, Z., Keating, E.H., Brown, C.F., 2015. Modeling the impact of carbon dioxide leakage into an unconfined, oxidizing carbonate aquifer. *International Journal of Greenhouse Gas Control*, (this issue)
- Cahill, A.G., Jakobsen, R., 2013. Hydro-geochemical impact of CO₂ leakage from geological storage on shallow potable aquifers: A field scale pilot experiment. *International Journal of Greenhouse Gas Control*, 19: 678-688.
- Cahill, A.G., Jakobsen, R., Mathiesen, T.B., Jensen, C.K., 2013. Risks attributable to water quality changes in shallow potable aquifers from geological carbon sequestration leakage into sediments of variable carbonate content. *International Journal of Greenhouse Gas Control*, 19(0): 117-125.
- Cahill, A.G., Marker, P., Jakobsen, R., 2014. Hydrogeochemical and mineralogical effects of sustained CO₂ contamination in a shallow sandy aquifer: A field-scale controlled release experiment. *Water Resources Research*, 50(2): 1735-1755.
- Caritat, P.d., Hortle, A., Raistrick, M., Stalvies, C., Jenkins, C., 2013. Monitoring groundwater flow and chemical and isotopic composition at a demonstration site for carbon dioxide storage in a depleted natural gas reservoir. *Applied Geochemistry*, 30(0): 16-32.
- Carroll, S., Hao, Y., Aines, R., 2009. Geochemical detection of carbon dioxide in dilute aquifers. *Geochem.Trans.*, 10(4): <http://www.geochemicaltransactions.com/content/10/1/4>.
- Celia, M.A., Nordbotten, J.M., 2009. Practical modeling approaches for geological storage of carbon dioxide. *Ground Water*, 47(5): 627-638.
- Dafflon, B. et al., 2013. Monitoring CO₂ Intrusion and Associated Geochemical Transformations in a Shallow Groundwater System Using Complex Electrical Methods. *Environmental Science & Technology*, 47(1): 314-321.
- Dai, Z.X. et al., 2014. Probabilistic evaluation of shallow groundwater resources at a hypothetical carbon sequestration site. *Scientific Reports*, 4.
- Damen, K., Faaij, A., van Bergen, F., Gale, J., Lysen, E., 2005. Identification of early opportunities for CO₂ sequestration-worldwide screening for CO₂-EOR and CO₂-ECBM projects. *Energy*, 30(10): 1931-1952.
- Frye, E., Bao, C., Li, L., Blumsack, S., 2012. Environmental Controls of Cadmium Desorption during CO₂ Leakage. *Environmental Science & Technology*, 46(8): 4388-4395.
- Gilfillan, S.M.V., Haszeldine, R.S., 2011. Comment on "Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers". *Environ. Sci. Technol.*, 45(7): 3171-3174.
- Harvey, O., Qafoku, N.P., Cantrell, K., Wilkins, M., Brown, C.F., 2015. CO₂-stimulated autotrophic methanogenesis: Implication for CO₂ sequestration and metal mobility in sulfide mineral systems. *Geochimica et Cosmochimica Acta* (submitted).
- Harvey, O.R. et al., 2013. Geochemical Implications of Gas Leakage associated with Geologic CO₂ Storage-A Qualitative Review. *Environmental Science & Technology*, 47(1): 23-36.
- Holloway, S., Pearce, J.M., Hards, V.L., Ohsumi, T., Gale, J., 2007. Natural emissions of CO₂ from the

- geosphere and their bearing on the geological storage of carbon dioxide. *Energy*, 32(7): 1194-1201.
- Humez, P., Lagneau, V., Lions, J., Negrel, P., 2013. Assessing the potential consequences of CO₂ leakage to freshwater resources: A batch-reaction experiment towards an isotopic tracing tool. *Applied Geochemistry*, 30: 178-190.
- Jordan, P., Benson, S., 2009. Well blowout rates and consequences in California Oil and Gas District 4 from 1991 to 2005: implications for geological storage of carbon dioxide. *Environ. Geol.*, 57(5): 1103-1123.
- Keating, E.H. et al., 2011. The challenge of predicting groundwater quality impacts in a CO₂ leakage scenario: Results from field, laboratory, and modeling studies at a natural analog site in New Mexico, USA. 10th International Conference on Greenhouse Gas Control Technologies, 4: 3239-3245.
- Keating, E.H. et al., 2013a. CO₂ leakage impacts on shallow groundwater: Field-scale reactive-transport simulations informed by observations at a natural analog site. *Applied Geochemistry*, 30: 136-147.
- Keating, E.H. et al., 2013b. CO₂/Brine Transport into Shallow Aquifers along Fault Zones. *Environmental Science & Technology*, 47(1): 290-297.
- Keating, H.E., Fessenden, J., Kanjorski, N., Koning, D.J., Pawar, R., 2010. The impact of CO₂ on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration. *Environmental Earth Science*, 60(3): 521-536.
- Kharaka, Y.K. et al., 2010a. Geologic storage of carbon dioxide: Potential environmental impacts of CO₂-organic interactions. *Geochimica et Cosmochimica Acta*, 74(12): A511-A511.
- Kharaka, Y.K. et al., 2010b. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environ. Earth Sci.*, 60: 273-284.
- Kirsch, K., Navarre-Sitchler, A.K., Wunsch, A., McCray, J.E., 2014. Metal Release from Sandstones under Experimentally and Numerically Simulated CO₂ Leakage Conditions. *Environmental Science & Technology*, 48(3): 1436-1442.
- Lawter, A., Qafoku, N.P., Wang, G., Shao, H., Brown, C.F., 2015. Evaluating and Predicting Impacts of CO₂ Intrusion into a Confined Sandstone Aquifer: 1. Experimental Data. (*International Journal of Greenhouse Gas Control* (this issue)).
- Lewicki, J.L., Birkholzer, J., Tsang, C.F., 2007. Natural and industrial analogues for leakage of CO₂ from storage reservoirs: identification of features, events, and processes and lessons learned. *Environ. Geol.*, 52(3): 457-467.
- Little, M.G., Jackson, R.B., 2010a. Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers. *Environmental Science & Technology*, 44(23): 9225-9232.
- Little, M.G., Jackson, R.B., 2010b. Potential impacts of leakage from deep CO₂ geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.*, 44(23): 9225-9232.
- Lu, J., Partin, J., Hovorka, S., Wong, C., 2010. Potential risks to freshwater resources as a result of leakage from CO₂ geological storage: a batch-reaction experiment. *Environmental Earth Sciences*, 60(2): 335-348.
- Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., 2005. Carbon Dioxide Capture and Storage-Special Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge.
- Montes-Hernandez, G., Renard, F., Lafay, R., 2013. Experimental Assessment of CO₂-Mineral-Toxic Ion Interactions in a Simplified Freshwater Aquifer: Implications for CO₂ Leakage from Deep Geological Storage. *Environmental Science & Technology*, 47(12): 6247-6253.
- Musgrove, M., Fahlquist, L., Houston, N.A., Lindgren, R.J., Ging, P.B., 2010. Geochemical evolution processes and water-quality observations based on results of the National Water-Quality Assessment Program in the San Antonio segment of the Edwards aquifer, 1996-2006.
- Navarre-Sitchler, A.K., Maxwell, R.M., Siirila, E.R., Hammond, G.E., Lichtner, P.C., 2013. Elucidating geochemical response of shallow heterogeneous aquifers to CO₂ leakage using high-

- performance computing: Implications for monitoring of CO₂ sequestration. *Advances in Water Resources*, 53: 45-55.
- Nordbotten, J.M., Celia, M.A., Bachu, S., Dahle, H.K., 2005. Semianalytical solution for CO₂ leakage through an abandoned well. *Environ. Sci. Technol.*, 39(2): 602-611.
- Peter, A. et al., 2012. Investigation of the geochemical impact of CO₂ on shallow groundwater: design and implementation of a CO₂ injection test in Northeast Germany. *Environmental Earth Sciences*, 67(2): 335-349.
- Qafoku N.P. AR Lawter, H Shao, G Wang, CF Brown. 2014. Evaluating Impacts of CO₂ Gas Intrusion Into a Confined Sandstone aquifer: Experimental Results. *Energy Procedia*, 63: 3275-3284
- Qafoku, N.P. et al., 2013. Geochemical Impacts of Leaking CO₂ from Subsurface Storage Reservoirs to Unconfined and Confined Aquifers. PNNL-22420, Pacific Northwest National Laboratory.
- Qafoku, N.P., Dresel, E.P., Ilton, E., McKinley, J.P., Resch, C.T., 2010. Chromium(VI) transport in an acidic waste contaminated subsurface medium: The role of reduction *Chemosphere*, 81: 1492-1500.
- Scherer, G.W., Kutchko, B., Thaulow, N., Duguid, A., Mook, B., 2011. Characterization of cement from a well at Teapot Dome Oil Field: Implications for geological sequestration. *Int. J. Greenhouse Gas Control*, 5(1): 115-124.
- Skinner, L., 2003. CO₂ blowouts: An emerging problem : Well control and intervention, 224. Gulf, Houston, TX, ETATS-UNIS, 4 pp.
- Smyth, R.C. et al., 2009. Assessing risk to fresh water resources from long term CO₂ injection-laboratory and field studies. *Energy Procedia*, 1(1): 1957-1964.
- Spangler, L.H. et al., 2010. A shallow subsurface controlled release facility in Bozeman, Montana, USA, for testing near surface CO₂ detection techniques and transport models. *Environmental Earth Sciences*, 60(2): 227-239.
- Trautz, R.C. et al., 2013. Effect of Dissolved CO₂ on a Shallow Groundwater System: A Controlled Release Field Experiment. *Environmental Science & Technology*, 47(1): 298-305.
- Varadharajan, C. et al., 2013. A laboratory study of the initial effects of dissolved carbon dioxide (CO₂) on metal release from shallow sediments. *International Journal of Greenhouse Gas Control*, 19: 183-211.
- Wang, S., Jaffe, P.R., 2004. Dissolution of a mineral phase in potable aquifers due to CO₂ releases from deep formations; effect of dissolution kinetics. *Energy Convers. manage.*, 45(18-19): 2833-2848.
- Wilkin, R.T., Digiulio, D.C., 2010. Geochemical impacts to groundwater from geologic carbon sequestration: controls on pH and inorganic carbon concentrations from reaction path and kinetic modeling. *Environ. Sci. Technol.*, 44: 4821-4827.
- Yang, Q. et al., 2014. Groundwater hydrogeochemistry in injection experiments simulating CO₂ leakage from geological storage reservoir. *International Journal of Greenhouse Gas Control*, 26(0): 193-203.
- Zheng, L.G. et al., 2012. Geochemical modeling of changes in shallow groundwater chemistry observed during the MSU-ZERT CO₂ injection experiment. *International Journal of Greenhouse Gas Control*, 7: 202-217.

Table 1. The Edwards aquifer synthetic groundwater preparation based on USGS groundwater data from the Edward aquifer

	Cations [mmol/L]				Anions [mmol/L]		
	Calcium	Magnesium	Sodium	Carbonate	Chloride	Sulfate	Nitrate
USGS ¹	2.7696	0.3966	0.3402	2.9	0.4344	0.152	0.0371
SGW	2.7696	0.3966	0.3402	2.7696	0.3966	0.1701	0.2911

¹Musgrove et al. (2010); the SGW synthesis was focused on elements Ca, Mg, K, Na, Cl, S and N and used the 75th percentile from the USGS data as the basis for the recipe.

Table 2. Selected column parameters and the solid materials used in each column experiment

Experiment Set	Material	Column Dimension	Porosity [-]	Flow Rate [mL/min]	Sample Preparation	Flow Fluid
Set 1, Column 1	Accusand	ID 2.49 x 15.2 cm	0.17		<2 mm	Synthesized Edwards ground water with N ₂ /CO ₂ purging (0.5 mL/min] under 0.5 PSI headspace pressure in reservoir
Set 1, Column 2	Accusand and Sample 1	ID 2.49 x 15.2 cm	0.17/0.27		Hammer- crashed to <2 mm	
Set 2, Column 1	Sample 1	ID 2.4 x 5.7 cm	0.25	0.024		
Set 2, Column 2	Sample 3	ID 2.4 x 5.7 cm	0.27	0.03		
Set 3, Column 1	Sample 4	ID 2.4 x 5.7 cm	0.26	0.031		
Set 3, Column 2	Sample 5	ID 2.4 x 5.7 cm	0.36	0.022	Sieved to <2 mm	

Table 3. XRD results from the collected Edwards aquifer samples

Sample	Size	Calcite	Quartz	Montmorillonite
Sample 1	< 2 mm	100%	-	-
Sample 2	< 2 mm	100%	-	-
Sample 3	< 2 mm	100%	-	-
Sample 4	< 2 mm	19.9%	36.4%	43.8%
	< 53 μm	54.5%	33.3%	12.1%
Sample 5	< 2 mm	1%	44.3%	54.7%
	< 53 μm	37.8%	38.6%	23.7%
Sample 6	< 2 mm	77.9%	7.9%	14.2%
	< 53 μm	98.1%	1.9%	-

Table 4: The detected minor and trace elements in all sample experiments after up to 14 days reaction with and without CO2-exposed conditions in the batch experiments. The values indicate the maximum concentrations observed in the entire test, and the values in parenthesis represent without CO2-exposed conditions.

Elements	As	Cu	Mn	Mo	Cs	Cd	Fe	Pb	S	Sn	Cr
	(µg/L)	(µg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	(mg/L)	(µg/L)
Sample 1	30.3 (28.6)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	8.1 (5.8)	0.9 (ND)	ND (ND)
Sample 2	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	8.9 (7.6)	1.6 (ND)	ND (ND)
Sample 3	47.9 (43.1)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	20.5 (21.7)	1.5 (ND)	ND (ND)
Sample 4	ND (ND)	2.56 (ND)	0.2 (ND)	0.9 (ND)	0.03 (ND)	ND (ND)	ND (ND)	ND (ND)	7.3 (6.2)	0.9 (ND)	1.96 (3.06)
Sample 5	ND (ND)	ND (ND)	3.5 (ND)	ND (ND)	0.7 (0.5)	7.6 (ND)	ND (ND)	ND (ND)	8.5 (7.5)	ND (ND)	ND (ND)
Sample 6	ND (ND)	6.99 (ND)	0.2 (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	ND (ND)	NR (NR)	1.0 (0.6)	ND (ND)

Table 5. Data from Set 2 and 3 of column experiments conducted with Edwards aquifer samples 1, 3, 4 and 5. The ND symbol is used to denote a non-detectable concentration. The numbers in parentheses in the first column are the secondary drinking water standards for selected contaminants in drinking water for public supply systems.

Contaminant	EPA Maximum Contaminant Level (MCL in µg/L)	Sample 1	Sample 3	Sample 4	Sample 5	ICP-EOS/MS Experimental Quantitative Limit (=detection limit *dilution factor)
Aluminum	(50-200)	2 - 37	4 - 88	7 - 37	1 - 9	165 // 82.4** (OES)
Arsenic (As)	10	0.2 - 24	0.2 - 45	0.1 – 62.5	0.1 – 45.1	4.68 (MS)
Barium (Ba)	2000	3.8 - 203	5.1 - 166	30.9 - 379	2.7 – 389.4	0.624 (MS) // 18.2 ** (OES)
Beryllium	4	ND	ND	ND	ND	23.7
Cadmium (Cd)	5	< 0.14	< 0.16	< 0.15	< 0.73	1.01 (MS)
Chloride (Cl)	(250000)	ND	ND	ND	ND	
Chromium (Cr)	100	0.4 – 12.4	0.4 – 18.1	0.3 – 1.6	0.1 – 5.1	1.92 (MS)
Copper (Cu)	(1000)	0.5 – 5.4	0.7 – 58.2	ND	0.6 – 27.9	4.37 (MS)
Iron (Fe)	(300)	ND	ND	ND	ND	100
Lead (Pb)	15	0.1 – 97	0.1 - 817	0.1 – 125.2	0.01 – 34.2	0.93 (MS)
Manganese (Mn)	(50)	5.3 - 13	0 – 11.9	1.2 – 35.9	2.4 – 267.3	94.1 // 47.1** (OES)
Mercury (Hg)	2	ND	ND	ND	1.2 – 30.2	1.5 // 1.5 ** (MS)
Nickel (Ni)	ND	3.9 - 75	37 - 93	15.2 – 44.6	< 4.5	227 // 113.6 ** (OES)
Nitrate (NO3 as N)	10000	ND	ND	ND	ND	
Selenium (Se)	50	0.2 - 81	0.4 - 150	0.1 – 190.9	ND	13.6 (MS)
Silver (Ag)	50; (100)	2.4 - 918	4.7 – 11.2	0.1 – 19.7	0.04 – 5.8	179 // 0.6 ** (MS107)
Sulfate (SO4)	(250000)	ND	ND	ND	ND	
Thallium (TI)	2	ND	ND	ND	ND	
Uranium	30	ND	ND	3 - 84	ND	
Zinc	(5000)	0 - 154	0 - 750	14.6 – 177.6	3.7 – 431.4	149.5 (OES)

** These value indicate the ICP-EOS/MS experimental quantitative limit (=detection limit *dilution factor) for sample 4 and 5 which were run with a different laboratory protocol than sample 1 and 3.

Figure 1. The schematic of the column experiment setup

Figure 2. Changes in pH with time in six Edwards Aquifer sediments exposed to CO₂ gas in batch experiments. The empty symbols represent the corresponding controls (i.e., blanks, which were not exposed to the CO₂ gas).

Figure 3. Changes in Ca concentration with time in six Edwards Aquifer sediments exposed to CO₂ gas in batch experiments. The empty symbols represent the corresponding controls (i.e., blanks, which were not exposed to the CO₂ gas).

Figure 4. Changes in Si concentration with time in three Edward aquifer materials exposed to CO₂ gas in the batch experiments. The empty symbols represent the corresponding controls (i.e., blanks, which were not exposed to the CO₂ gas).

Figure 5. Changes in effluent pH, Eh, Ca and Si concentrations during leaching with CO₂ saturated SGW. The pH and Eh measurements were taken on-line. The first column was packed with Accusand material (black) and the second column was packed partially with Accusand and partially with the Edwards aquifer sample 1 (red).

Figure 6. Changes in effluent pH and Ca, As and Pb concentrations as a function of time in two column experiments conducted with Edwards aquifer samples 1 (red) and 3 (black).

Figure 7. Changes in effluent pH, Eh and Ca, Si, Pb and Mo concentrations as a function of time in two column experiments conducted with Edwards aquifer samples 4 (red) and 5 (black).