Evaluating Impacts of CO₂ Intrusion into an Unconsolidated Aquifer: 1. Experimental Data[†]

Amanda Lawter^{*1}, Nikolla P. Qafoku¹, Guohui Wang¹, Hongbo Shao¹,
and Christopher F. Brown¹

¹Pacific Northwest National Laboratory (PNNL), Richland, WA

Submitted: December 2014

International Journal of Greenhouse Gas Control

*Author to whom correspondence should be addressed.

Address: Geosciences Group, Earth Systems Science Division, Pacific Northwest
National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MSIN: P7-54, Richland,
WA 99352

E-mail: amanda.lawter@pnnl.gov

Phone: (509) 375-2709

Fax: (509) 371-7249

[†] Electronic Supplementary Information (ESI) available.

ABSTRACT

Capture and deep subsurface sequestration of CO₂ has been identified as a potential mitigation technique for rising atmospheric CO₂ concentrations. Sequestered CO₂ represents a potential risk to overlying aquifers if the CO₂ leaks from the deep storage complex. Batch and column experiments combined with wet chemical extractions were conducted to evaluate these risks to groundwater quality and to understand effects of unintentional release of CO₂ on groundwater chemistry and aquifer mineralogy. Sediments from the High Plains aquifer in Kansas, a largely unconsolidated aquifer, were used to study time-dependent release of major, minor and trace elements when exposed to CO₂ gas. Results showed that Ca, Ba, Si, Mg, Sr, Na, and K increased either within the first four hours or followed nonlinear increasing trends with time, indicating that dissolution and/or desorption reactions controlled their release. In addition, other elements (e.g., Fe and Mn) and trace elements (e.g., As, Cu, Cr, Pb) were released during batch and column experiments, demonstrating the possibility for changes in mineralogy and groundwater quality degradation due to exposure to seepage of sequestered CO₂. National drinking water regulations were exceeded for As and Mn in the batch experiments, and As, Se, Mn, Pb and Hg in the column experiments, despite low levels of these contaminants found in the sediments. In addition, the concentration of another potential contaminant, i.e., Mo, was consistently higher in the control batch experiments (i.e., absence of CO₂) but was below detection in the presence of CO₂ indicating a potential for removal of elements by CO₂ gas exposure. Although results will be site specific for the High Plains aquifer and other mostly unconsolidated aquifers, these investigations will provide useful information to support site selection, risk assessment, and public education efforts associated with geological CO₂ storage and sequestration.

Keywords: CO₂ gas, groundwater contamination, contaminant release

1. INTRODUCTION

Mitigation of climate change includes decisive action to reduce concentrations of CO₂ gas in the atmosphere. Capturing CO₂ from large stationary sources such as coal-fired power plants and storing it in deep geologic formations (often referred to as geologic CO₂ sequestration or GCS) has been proposed as one viable option to mitigate future adverse effects of climate change (Bachu, 2000; Bruant et al., 2002; IPCC, 2005). However, concerns have been raised about possible impacts of unintentional release of CO₂ to shallow aquifers overlying the storage sites (Harvey et al., 2013).

For seepage of CO₂ from deep storage complexes, two release scenarios are possible (Bachu, 2008; Metz et al., 2005). The first is a sudden, fast, and short-lived release of CO₂. This scenario would occur in the case of well failure during injection or storage (due to corrosion of the casing or if the cement between the casing and the rock becomes weakened by the CO₂ gas), and/or rare instances of gas blowouts (Holloway et al., 2007; Jordan and Benson, 2009; Skinner, 2003). In the second scenario, 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). This slow, harder to detect release of CO₂ has the greatest potential to cause broad-scale environmental impacts (Bachu, 2008; Damen et al., 2005; Metz et al., 2005).

Studies on the potential effects of CO₂ release from deep geological storage reservoirs have recently increased; the topics covered include numerical simulation to predict the effect of CO₂ seepage (Bacon, 2013; Jacquemet et al., 2005; Navarre-Sitchler et al., 2013; Romanak et al., 2012; Wang and Jaffe, 2004; Zheng et al., 2009; Zheng et al., 2012), natural analogues (de Caritat et al., 2013; Keating et al., 2010; Lewicki et al., 2007), field studies involving in-situ CO₂

injection (Kharaka et al., 2010; Nisi et al., 2013; Peter et al., 2012; Smyth et al., 2009; Trautz et al., 2013), and experimental column and batch studies (Humez et al., 2013; Little and Jackson, 2010; Lu et al., 2010; Montes-Hernandez et al., 2013; Wang et al., 2014; Wei et al., 2011). However, the results of the studies are contradictory as some indicate CO₂ leaks pose a serious risk (Cahill et al., 2013; Kharaka et al., 2010; Little and Jackson, 2010; Lu et al., 2010; Vong et al., 2011; Wang and Jaffe, 2004; Wei et al., 2011; Zheng et al., 2009), and some indicate low levels of risk (Bacon et al., 2014; Frye et al., 2012; Keating et al., 2010; Kirsch et al., 2014; Mickler et al., 2013; Smyth et al., 2009; Wang et al., 2014). While a variety of studies of CO₂ and groundwater have been conducted, knowledge gaps still remain, including the effect of microbial activity, sediment mineralogy, and gas stream composition, studied in a way that allows for comparison across all variables through the use of agreed-upon testing protocols (Harvey et al., 2013).

A decrease in pH is expected in aquifers exposed to CO₂ due to the formation and disassociation of carbonic acid. This decrease in pH creates a potential for contaminant release (Little and Jackson, 2010; Vong et al., 2011; Wang and Jaffe, 2004; Zheng et al., 2009). Wang and Jaffe (2004) used numerical simulations with systems of galena and quartz, and galena and calcite to predict Pb concentration changes as a result of dissolution of PbS, and in a field study, Kharaka et al. (2010) reported increased levels of Pb due to CO₂ exposure, along with Fe, Mn, As, Cu, An, Cd, Al, and Se. Kirsch et al. (2014) found that the contaminants released in their laboratory experiments were directly correlated with calcite dissolution, leading them to conclude that calcite dissolution provides the source of the contaminants. A batch experiment conducted by Lu et al. (2010) also suggests aquifers containing carbonate rocks are of particular concern.

Kirsch et al. (2014) found calcite to be the source of potential risks, but carbonate dissolution can also be beneficial for groundwater aquifers exposed to CO₂ as it buffers the system to avoid further decreases in pH (Cahill et al., 2013; Little and Jackson, 2010). In an analog study conducted in New Mexico, USA, Keating et al. (2010) reported that despite relatively high levels of dissolved CO₂, trace element mobility in calcite containing aquifers is not significant. They attributed this minor effect of CO₂ intrusion to the high buffering capacity of the groundwater aquifer they studied. In a column study, Frye et al. (2012) also observed that the geochemical properties of aquifer materials significantly influenced the response of groundwater quality to the intrusion of CO₂. They found that calcite content as low as 10% can mitigate the effect of pH reduction and may result in zero Cd desorption (Frye et al., 2012). Results of reaction path and kinetic models are in agreement with these laboratory and field studies, again emphasizing the importance of geochemical properties, and specifically the calcite content, of the aquifer (Wilkin and Digiulio, 2010). Despite detectable contaminant concentrations in their batch study, Kirsch et al. (2014) believe the low level of released contaminants during experiments also indicates a low risk for groundwater quality. Mickler et al. (2013) conducted laboratory batch experiments as well as a single-well push-pull field test and found that several of the elements initially mobilized after introduction of CO₂ (Mo, V, Zn, Se and Cd) were removed from the solution by the end of the experiment. Mickler et al. (2013) observed several other elements increased in concentration, but only Mn exceeded EPA Maximum Contaminant Levels (MCLs).

To further current knowledge, the objective of this study is to understand how unintentional release of CO₂ from storage complexes will influence the water quality in overlying unconsolidated aquifers with little or no calcite content. Specifically, we aim to study

1) aqueous phase pH and elemental composition changes with time and 2) mobilization of toxic trace elements to evaluate potential risks to groundwater in poorly consolidated aquifers due to CO₂ exposure. Sediments from various depths within the same well with differing mineralogy were used to observe the effect of sediment composition on pH buffering ability and subsequent contaminant release. Batch experiments were conducted to simulate sudden, short-lived CO₂ release and column experiments were conducted to simulate the effect of gradual leaks of CO₂. The results from this research will support site selection, risk assessment, policy-making, and public education efforts associated with geologic carbon sequestration.

2. MATERIALS AND METHODS

2.1 High Plains Sediments

Sediment samples were obtained from the High Plains aquifer in Kansas from the Drill Core Library at the Kansas Geological Survey (maps are included in the Electronic Supplementary Information [ESI], Fig. S1). In this area, the High Plains aquifer is comprised of largely unconsolidated sand, gravel, and silt, with caliche present discontinuously (Becker et al., 2002). The sediment samples were collected from the CNG well from depths of 8 feet to 151 feet. The CNG well is located in Morton County in southwest Kansas. The samples arrived as loose sediments and, if needed, underwent dry sieving to obtain the <2 mm fraction for characterization and batch and column experiments. Characterization tests were conducted for these sediment samples to determine the identity of minerals, chemical composition, and surface morphological features.

2.2 Acid Extractions

Acid extractions were performed for <2mm sieved sediment samples using 8 M nitric acid. The sieving and acid extractions were conducted on air-dried samples as received. Other size fractions (53 μ m-2 mm and <53 μ m) were separated for additional acid extractions. The moisture content of each sediment sample was measured in triplicate to correct for the weight of the moisture in the calculation of acid extraction results. To conduct the extraction, one gram of sample and 5 mL of 8 M nitric acid were mixed in a 15 mL centrifuge tube, and transferred to a polypropylene tube. An additional 1 mL aliquot of 8 M nitric acid was used to rinse the centrifuge tubes to ensure all solid was transferred from the centrifuge tube. The polypropylene tubes were heated to 95 °C for 2 hours, then transferred back to the centrifuge tube and centrifuged at 3500 rpm for 10 minutes. The supernatant was filtered through a 0.22 μ m syringe filter. The liquid was submitted for inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses. ICP-MS and ICP-OES analyses were performed using a Thermo Scientific X-series II and Perkin Elmer Optima 3300 DV and 8300 DV, respectively. Additional information on the ICP-MS and ICP-OES analyses and quality control procedures can be found in the ESI.

2.3 High Plains Sediments: SEM/EDS and Previous Characterization

These sediments have previously undergone characterization studies including soil texture, QXRD, and microwave digestion (Shao et al. 2014). To expand the understanding of these sediments, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) were conducted as well. SEM combined with EDS was used to characterize morphological features of sediment particles and determine the identity of possible adsorbents within the sediments based on particle chemical compositions. Individual clasts of the <52 μ m

fraction were carbon coated to make them electrically conducted and then examined using a JEOL 6340f SEM. Images were collected using a backscattered electron detector.

2.4 Synthetic Groundwater

Synthetic groundwater (SGW) was used in this work for both batch and column experiments. SGW was developed using USGS data for the composition of High Plains aquifer groundwater (Becker et al., 2002). Concentrations of major constituents (e.g., Ca, Mg, Na, Cl, CO_3 and SO_4) were based on the median reported values. CaCO_3 and MgCO_3 were dissolved in 2% nitric acid before being added to the groundwater to ensure complete dissolution. The final pH of the SGW was adjusted to 7.50 with 1 M KOH. The recipe for the SGW is included in the ESI.

2.5 Batch Experiments

A series of batch experiments were conducted to study major, minor, and trace element mobilization from sediments. Four sediments collected from the CNG well at depths of 8-9' (CNG 8), 60-61' (CNG 60), 110-111' (CNG 110), and 150-151' (CNG 150) were used in the batch study. According to the USGS, depth to the water table within the central High Plains aquifer ranged from less than one foot to over 500 feet, and the depth to water in the Kansas wells selected for the 1999 water quality assessment testing ranged from 15 to 350 feet (Becker et al., 2002). Batch reactors were prepared for this experiment by creating an inlet and small outlet port in the lid of 125mL poly bottles to allow CO_2 entry without pressure buildup, as shown in the ESI (Fig. S2). After adding 5g of the solid materials and 15 mL SGW to each reactor, the reactors were left overnight to equilibrate before being exposed to 99.9% CO_2 gas. CO_2 gas was injected continuously into the batch reactors. The gas rate (70 ± 10 mL/min) was monitored throughout all batch experiments (ESI Table S1). The relatively higher CO_2 flow rate

was chosen to ensure the saturation of CO₂ in the SGW, which would not limit the reactions that occurred in the course of these experiments. The elapsed experimental times were 0 hours (no gas injection), 4, 8, and 12 hours, and 1, 2, 3, 7, and 14 days. For each time, duplicate runs with continuous CO₂ flow and one control reactor were conducted simultaneously. Each control reactor received the same amount of sediment and SGW as the experiment reactors, but no gas was injected into these reactors. At the end of each experiment, the reactor was weighed, and a pH aliquot was removed and measured immediately. The remaining liquid was centrifuged and filtered through a 0.22 µm syringe filter. An aliquot of aqueous sample was acidified with concentrated nitric acid for elemental analyses with ICP-MS and -OES. Starting and ending weights showed that the loss of liquid and solid was negligible (less than 5%), except for the 14-day experiment where losses of 0.62-1.75 g (or mL) were observed. To minimize the loss of liquid, the CO₂ gas first flowed through a gas washing bottle filled with SGW, hydrating the gas before it flowed into the individual reactors.

2.6 Column Experiments

Details of column experiments are provided in Table 2. Two sediments (CNG 110 and CNG 60, <2 mm) from the High Plains aquifer were used in this study. A control column was packed with Accusand and was leached under conditions similar to those containing the sediments. A picture of the apparatus used in the column experiment is shown in the ESI (Fig. S3). Polyvinyl chloride (PVC) columns with inner diameter of 2.4 cm and length of 5.7 cm were packed using the method described in Qafoku et al. (2010).

The High Plains aquifer SGW (pH = 7.50) was used as the influent in these column experiments. The SGW was boiled for half an hour to cause de-aeration, and was then stored inside an anaerobic chamber overnight before use. All experiments were conducted under

hydraulically saturated condition. The de-aerated SGW was injected continuously into the columns from the bottom inlet using a KLOEHN V6 syringe pump at a flow rate of about 0.03 mL/min (0.40 cm/h). The experiments were conducted at room temperature (21 ± 2 °C), and the effluent pH and Eh were continuously measured in line using an Accumet benchtop XL15 pH and Eh meter. The solution Eh was determined by following the PNNL Technical Procedure (Document No.: AGG-Eh-001) in which the standard potential of the Pt electrode is determined using quinhydrone.

The columns were initially leached with SGW for several days to achieve hydrological equilibrium (i.e., full saturation) and were then leached with CO₂ gas-saturated SGW. CO₂ gas was continuously purged in the influent bottle at a rate of 0.5 mL/min. Two stop flow events were conducted after leaching with the CO₂ gas-saturated began. Stop flow conditions were used to determine the effect of increased fluid residence time on elemental release to observe time-dependent reactions and processes in the columns. One pH measurement per hour was conducted during continuous flow and one measurement per 15 minutes was performed immediately after the stop-flow events. Stop flow conditions were applied after the initial leaching with SGW prior to CO₂ injection (time = 70 hours, stopped for 170 hours) then twice more at approximately 250 hours and 350 hours, with the stop flows lasting 122 hours. During the experiment, about one sample per pore volume (PV) was collected, while the effluent samples were collected more frequently after the stop-flow events. At the end of the experiments, selected effluent samples were analyzed by both ICP-OES and -MS to determine the aqueous concentrations of major, minor, and trace elements.

3. RESULTS AND DISCUSSION

3.1 Sediment Characterization: Acid Extractions

Acid extractions were conducted to determine the chemical composition of the High Plains sediments. The results shown in Table 3 clearly indicate the sediments have detectable amounts of trace metals that are of environmental concern, such as As, Cd, Cr, and Pb which are regulated by the EPA with primary MCLs, and Fe, Mn, and Zn which are regulated with secondary MCLs (U.S.EPA, 2009). Importantly, these trace elements may potentially be released from High Plains sediments when they are exposed to CO₂ gas should it leak from deep subsurface storage complexes.

3.2 Sediment Characterization: QXRD and SEM/EDS

Calcite contents of sediments CNG 8, CNG 60, CNG 110, and CNG 150 were determined by QXRD. QXRD results of these sediments, which are included in a previous report (Qafoku et al., 2013) also showed the sediments contained appreciable amounts of feldspars, montmorillonite, quartz, and mica. CNG 8 contained 2.6% calcite, while CNG 110 contained 1.0% calcite and CNG 150 contained 4.1% calcite (Qafoku et al., 2013). CNG 60 contained no detectable carbonates, although a small amount may be present below detection limits (see Zheng et al., 2015, this issue). In addition to the QXRD analyses, we performed a series of SEM inspections and EDS measurements to characterize the morphology of the mineral particles and determine their chemical composition. EDS results show a low amount of Ca and high concentration of Si for CNG 60 (Fig. 1). These results are similar to the other CNG sediments obtained from the High Plains aquifer, although the other CNG sediments have been shown to contain higher amounts of calcite by QXRD (Qafoku et al., 2013) and SEM/EDS (Fig. 1). The SEM images show the samples have rough surfaces (Fig. 1). Rough surfaces can be indicative of high reactive

surface area and potentially high dissolution rates, and are also more likely to stimulate adsorption than smooth surfaces. EDS results, in agreement with previous QXRD data, suggest the presence of feldspars and/or micas in the High Plains aquifer CNG sediments.

3.3 Result from batch experiments

A comparison of results from batch tests conducted under constant CO₂ gas exposure with four sediments from the High Plains aquifer CNG sediments follows (see ESI, Fig. S4 to S7 for complete results). The pH decreases significantly in the three tests conducted with the sediments that contained calcite (CNG 8, CNG 110, and CNG 150; pH = 6.08–6.11), and is even more acidic (pH = 5.37) in the test conducted with the calcite-free sediment, CNG 60 (Fig. 2). The pH measured in the blank reactors ranged from approximately 7.2 to 8.2 at the start of the experiment. Although not significant, the pH in the blank reactors decreased slightly through the 15 days of the experiment, ending only slightly higher than the pH of the SGW (around 7.6).

The changes in aqueous Ca concentrations in response to CO₂ gas exposure are, as expected, more pronounced in the sediments that contain calcite (CNG 8, CNG 110, and CNG 150; average Ca concentration varied between 385 and 483 mg/L) than in the sediment that did not contain XRD detectable calcite (CNG 60; Ca average concentration of 113 mg/L) (Fig. 3). Calcite coatings and/or adsorbed/exchangeable Ca may have been present in the sediment CNG 60 but below the 1-5% detection limit for crystalline minerals via XRD. For sediments with calcite, the average Ca concentration was 3 to 5 times greater in the CO₂ exposed reactors than in the control reactors absent of CO₂ (Ca average concentration of 80 to 152 mg/L). The average concentration in CNG 60 with CO₂ present was less than two times that of the control reactor with the same sediment (Ca average concentration of 73 mg/L). The Ca concentration in all blanks was slightly higher than that measured in the SGW (Ca concentration of 47 to 52 mg/L).

The calcite concentration of aquifer sediments is important as it can indicate the ability of the aquifer to buffer against pH induced aqueous phase release of contaminants, as shown throughout the results of this study.

The dissolution of Si-bearing solid phases is also demonstrated in these experiments as the Si concentration increases significantly in the experiments conducted in the presence of the CO₂ gas. The greatest amount of Si is measured in the shallower CNG 8 sediment (a maximum of about 30 mg/L). No Si was detected in the SGW, but the Si concentration in the blanks increased while remaining lower than the CO₂ exposed experiments (Fig. 4).

Appreciable amounts of additional major elements, such as Ba, Sr, Mg, Na, and K, were mobilized in all sediments; the aqueous concentrations follow a non-linear increasing trend as a function of time (Fig. 5, Fig. S4-S7). Importantly, the aqueous concentrations of major divalent cations, such as Ba, Sr, and Mg, were lower in experiments conducted with CNG 60, the calcite-free sediment. This could be due to impurities of these cations in the calcite present in the sediments. This possibility is further discussed in the accompanying modeling paper (Zheng et al., 2014). Potassium concentrations for both the CO₂ exposed reactors and the blank reactors fell below the concentration of K in the SGW, as did the Mg concentration in the blank reactors for CNG 60, 110, and 150, and the CO₂ exposed reactors for CNG 60.

Minor elements were also released into the aqueous phase after exposure to CO₂. For example, Mn was mobilized from all sediments exposed to CO₂, but the Mn concentration fell below detection limits in the CNG 60 reactors for all but three sampling times; the maximum Mn concentration measured was approximately 500 µg/L in CNG 110 (Fig. 5). Mn was not detected in any of the blank reactors or the SGW. Slightly (but not significantly) greater S concentrations were present in the experiments exposed to CO₂ gas. Aqueous phase Fe was also detected once

in CO₂ injected samples conducted with CNG 110 (t = 12 h), and CNG 150 (t = 4 h), and twice in CNG 60 (t = 8 h, 14 d), suggesting Fe-bearing mineral dissolution and possible fast precipitation of secondary phases which may induce changes in Fe mineralogy of the sediments.

Detectable aqueous concentrations of Mo were present in all blanks and at time zero in CNG 8, CNG 60, and CNG 110, with averages ranging from 2.4 µg/L to 9.4 µg/L. However, Mo concentrations were not measured above the instrument detection limit (EQL = 1.3 µg/L) in the experiments conducted in the presence of the CO₂ gas for CNG 8, CNG 60, and CNG 110. In CNG 150 tests, the Mo concentration decreased significantly after CO₂ exposure and was consistently lower than the concentrations measured in the blanks (Fig. 5). Molybdenum is often associated with Fe oxides and/or sulfides (Smedley et al., 2014). Peak Mo adsorption on Fe oxides occurs around pH 4 and decreases rapidly with increasing pH (Goldberg et al., 1996). The pH was consistently above 7.5 in the blank reactors and around or below pH 6 in the CO₂ injected reactors, which suggests Fe oxides were the source of Mo detected in the blank experiments. The Mo aqueous phase decrease in the CO₂ injected reactors demonstrates potential for removal of contaminants from the aquifer with CO₂ gas exposure.

The CNG sediments containing calcite did not mobilize detectable concentrations of trace elements, with the exception of Cu, in the equilibration sample (t = 0) of CNG 150. Potential contaminants, including P, As, Cu, Cr, and Pb were detected occasionally in the aqueous phase in CNG 60 samples (Fig. 6). Importantly, these occurrences are in the calcite-free sediment. In a previous study conducted by our research team with sediments from a different well within the High Plains aquifer, it was reported that, similarly to the result presented in this paper, release of potential contaminants occurred more frequently in the experiment with no detectable calcite in the sediment compared to the sediments with calcite (Qafoku et al., 2014).

3.4 Result from column experiments

Column experiments were conducted with two of the sediments used in the batch study, CNG 60 and CNG 110. The effluent pH of both columns initially increased from approximately 6.3 to values between 7.2 and 7.4, which were similar to the pH of the inlet solution (7.5), but then decreased significantly to pH values of approximately 5.0 and 6.5 after the CO₂ gas-saturated SGW was injected into the column (Fig. 7). The pH measured in the batch experiments conducted with the same sediments were similar (CNG 60: 5.37; CNG 110: 6.09). In both the batch experiments and column experiments, CNG 60 exhibited less buffering capacity than CNG 110. During the experiment, the Eh of both columns increased significantly following the injection of CO₂ into the SGW (Fig. S8).

The effluent chemical composition of these columns changed significantly during the experiments (Fig. 3 and ESI Fig. S8). The Ca concentration decreased slightly in both columns during leaching with SGW. As seen in Fig. 7, the Ca concentration then increased significantly in the experiment conducted with CNG 60 (up to about 200 mg/L) and then decreased, reaching an apparent steady state concentration at about 50 mg/L. The effluent Ca concentration in the CNG 110 column was variable during leaching with CO₂ gas-saturated SGW, but was consistently higher than the Ca concentration in the effluent of the CNG 60 column. The batch experiment also resulted in higher Ca concentrations in CNG 110 than in CNG 60 (113mg/L vs. 393 mg/L). The Ca concentration did not change significantly during the stop-flow events, most likely indicating that a cation exchange reaction rather than dissolution was controlling the effluent Ca concentration in the CNG 60 column.

The Si concentration peaked after each stop flow event, and then decreased to low levels by the end of each flow event (Fig. 7). The peak decreased with each subsequent flow event. The

consistent decrease in Si concentration is consistent with the fact that the Si source controlling and contributing to the Si concentration in the pore water of both columns was mass limited. As the solid source began to deplete, the Si peak concentrations decreased. The solid source was most likely distributed throughout the sample matrix because the effluent concentration was a function of the fluid residence time; it increased during the stop-flow 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.

Aqueous concentrations of major divalent cations were lower in experiments conducted with sediment CNG 60 than in the experiments conducted with sediment CNG 110. In the column experiments the Sr effluent concentration was definitely greater in CNG 110; the changes in column effluent concentrations of Ba and Mg followed similar trends (Fig. 7). Again, this increase in divalent cations in CNG 110 compared to CNG 60 could be due to impurities in the calcite, as discussed in Zheng et al. (2014).

CNG 110 released a greater amount of Mn in the batch experiments than detected in the batch experiment for CNG 60. The maximum effluent concentration of Mn was greater in CNG 110 than in CNG 60 in the column experiments as well (Fig. 8). While Mn was only detected in three samples during the batch experiment, Mn was consistently detected throughout the column experiment.

Results show higher concentrations in the column experiment than in the batch experiment for other elements, such as P (3.1 mg/L vs. an average of 0.9 mg/L) and Al (maximum of approximately 500 µg/L vs. 227 µg/L). Additional elements detected in the CNG 60 column study include Mg (50 mg/L), Mn (500 µg/L), Hg (2 mg/L), Ag (30 µg/L), and S (14 mg/L) (Fig. 8, S8). CNG 110 effluents also contained Hg, P, and Ag but at lower concentrations

than found in CNG 60. The relatively high concentration of mercury deserves further investigation. Concentrations of Mg in CNG 110 column effluents were greater than in CNG 60, and the levels of Na and S in both columns were roughly the same.

Several trace elements were detected in the column study effluent samples, including Sb, Cr, Se, As, Pb, Cs, Cu, and Zn. Other trace elements, including Bi, Cd, Li, Ni, and Zr were detected by the instrument used to run the analyses, but concentrations fell below the detection limit of the ICP. Trace elements with effluent concentrations above the detection limit only during leaching with the SGW prior to CO₂ saturation and/or immediately following stop-flow events include Sb, Cr, Cu, Se, and Zn. Arsenic and Pb had effluent concentrations above the instrument detection limits in both columns (Fig. 8). Some of the elements were only above detection limits in one column, such as Al and Cs in the CNG 60 column. Levels of several trace elements were greater in the CNG 60 column study than the CNG 60 batch study, such as As (65 µg/L vs. an average 8.28 µg/L) and Pb (150 µg/L vs. 5.31 µg/L). As in the batch experiments, the levels of trace element contaminants were greater in the CNG 60 effluent samples than in the CNG 110 samples (Fig. 8). Arsenic and Pb concentrations exceeded EPA MCLs multiple times throughout the CNG 110 column study, but these MCLs were exceeded for a majority of the CNG 60 experiment. The differences between the column and batch experiments demonstrate the difference between these two fundamentally different experimental methods. Differences in the two sediments seem to be caused by the differing calcite content in each.

3.5 Discussion

Contamination of groundwater with trace metals was the major issue that we wanted to evaluate in our study to address potential risks associated with CO₂ seepage into potable aquifers. For this reason, we measured the aqueous concentrations of different elements to

compare them with the U.S. EPA MCLs (U.S.EPA, 2009). According to the National Drinking Water Regulations, MCLs are divided into two categories: primary and secondary. Primary drinking water standards, which include trace metals, such as As, Cd, and Pb, among others, are legally enforced for the protection of public health by limiting the levels of contaminants in drinking water. Secondary drinking water standards, which include standards for Fe, Mn, and Zn, are non-enforceable guidelines regulating contaminants that may cause undesirable cosmetic or aesthetic effects in drinking water.

The column and batch experiments conducted during this investigation have demonstrated the possibility of an increase in these elements of concern through mineral dissolution and/or cation exchange reactions driven by the addition of CO₂ into the system. However, release of these elements was sediment specific.

The sediments originated from a poorly consolidated aquifer dominated by quartz sand but some samples contained detectable amounts of calcite. Despite the low amounts of calcite in CNG 8, CNG 110, and CNG 150, this results in a large difference in buffering capability compared to CNG 60, where only very small amounts of Ca were detected by SEM/EDS, and no calcite was detected by QXRD. The increased release of trace elements such as As and Cs in CNG 60 experiments shows possible effects of a lack of buffering capability- these elements were likely released due to the lower pH values measured in the experiments conducted with the CNG 60 sediment compared to the pH values measured in other CNG sediments. The calcite content also demonstrated the possibility of additional elements being released during calcite dissolution, such as Ba, Sr, and Mg that either were part of the calcite crystal structure (i.e., impurities within the calcite structure), or were released as a result of exchange reactions triggered by increases in the aqueous Ca concentration as a result of calcite dissolution. This

explains why the calcite-free CNG 60 released lower concentrations of these elements in the aqueous phase after exposure to the CO₂ gas.

Additional batch and column experiments have already been conducted by our research group, with variables including brine concentration (0.1M or 1M NaCl), long term batch tests (119 days), CO₂ flow rate (50 to 350mL/min), and aquifer type, with results found in Qafoku et al. (2013) and Wang et al. (2014). The results from these experiments were similar to the results presented in this paper, also concluding that trace metals can be released by exposure to CO₂, although the rate and extent of release appears to be highly site specific.

Modeling development and calculations have also been conducted using data from the column experiments to better understand the mechanisms and pathways of contaminant release. The results from modeling showed that calcite dissolution, Ca-driven cation exchange reactions, and adsorption/desorption reactions to be the major drivers for concentration changes in this system (Zheng et al., 2014). Model results again emphasize the importance of calcite content, as well as CEC and sorption capacity as major sediment properties that may affect and/or control aqueous concentrations of the chemical elements released from mineral structures during these experiments and determine their ultimate fate. Exploration of a large range of variables is important as contamination of groundwater may require extensive remediation to comply with the EPA MCLs and the Safe Drinking Water Act. Largely unconsolidated aquifers such as the High Plains Aquifer may contain greater site-specific variability, and may require greater sampling and evaluation.

The results of this study are important because previous analog studies conducted in natural geologic complexes containing large amounts of CO₂ have shown that seepage pathways are possible and the exposure of aquifer sediments to excess amounts of CO₂ gas escaping from

deep subsurface storage complexes is likely. For example, Lewicki et al. (2007) summarized CO₂ leakage incidents from natural and industrial analogues revealing that in more than 20 examples worldwide, CO₂ escaped mainly through faults, fractures, and wells. Through these conduits, fugitive CO₂ may intrude into drinking water aquifers, causing a decrease in pH and a release of trace metals from dissolving minerals, as it was clearly demonstrated in the results of this and other studies. Results of this study as well as previous studies by Wilkin and Digiulio (2010) and Keating et al. (2010), among others, have emphasized the importance of aquifer mineralogy and geochemistry in determining risk to overlying groundwater aquifers if the CO₂ were to reach these underground sources of drinking water (USDW).

4. CONCLUSIONS

With the recognition that carbon capture and subsequent geologic CO₂ sequestration is a viable option for reducing the amount of CO₂ released into the atmosphere, risk analysis is an essential step in the process of safe geologic containment. Release of CO₂ into overlying aquifers causes a decrease in pH, providing the potential for mineral dissolution to cause a release of contaminants into the aquifer, affecting the quality of the groundwater. The batch and column experiments conducted have shown that changes in groundwater chemistry due to CO₂ exposure can be expected in the event of a leak of CO₂ from storage complexes into overlying aquifers. Major elements, such as Ca, Ba, and Si, were released from sediments in all experiments. The concentration of several minor elements also increased with exposure to CO₂, including Mn, Sr, P, and Fe. Mo concentrations trended in the opposite direction, with decreasing concentrations with CO₂ exposure. Importantly, several trace elements, determined by the EPA to affect groundwater quality, were released from sediment when exposed to CO₂ gas or

CO₂ gas saturated SGW, including As, Pb, Cu, and Cr. In the batch study, the concentration of As exceeded the MCL at only one sampling time. In the column studies, Pb and As concentrations exceeded the MCLs in both sediment columns multiple times throughout the experiment. Batch and column experiments have shown that the amount of calcite in the sediment can have a strong effect on buffering capabilities. Presence of calcite in sediments can buffer aquifers and mobilize fewer contaminants, compared to other sediments that have undetectable amounts of calcite. The correlation shows the importance of conducting site specific assessments; our experiments have shown high variability between sediment samples even within the same well.

ACKNOWLEDGEMENTS

Funding for this research was provided by the National Risk Assessment Partnership (NRAP) in the U.S. DOE Office of Fossil Energy under DOE contract number DE AC05 76RL01830. XRD and SEM analysis were performed in the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL. PNNL is operated by Battelle for the U.S. DOE under Contract DE-AC06-76RLO 1830. Samples were obtained from the Kansas Geological Survey at Kansas University.

REFERENCES

- Annunziatellis, A., Beaubien, S. E., Bigi, S., Ciotoli, G., Coltella, M., and Lombardi, S. (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**, 353-372.
- Bachu, S. (2000). Sequestration of CO₂ in geological media: criteria and approach for site selection in response to climate change. *Energy Convers. Manage.* **41**, 953-970.
- Bachu, S. (2008). CO₂ storage in geological media: Role, means, status and barriers to deployment. *Prog. Energy Combust. Sci.* **34**, 254-273.
- Bacon, D. (2013). Reduced Order Model for the Geochemical Impacts of Carbon Dioxide, Brine, and Trace Metal Leakage into an Unconfined, Oxidizing Carbonate Aquifer, Version 2.1. *NRAP REPORT PNNL-22285, Pacific Northwest National Laboratory*.
- Bacon, D., Qafoku, N. P., Dai, Z., Keating, E. H., and Brown, C. F. (2014). Modeling the impact of carbon dioxide leakage into an unconfined, oxidizing carbonate aquifer. *International Journal of Greenhouse Gas Control* (submitted)
- Becker, M. F., Bruce, B. W., Pope, L. M., and Andrews, W. J. (2002). "Ground-Water Quality in the Central High Plains Aquifer, Colorado, Kansas, New Mexico, Oklahoma, and Texas, 1999." U.S. Geological Survey.
- Bruant, R. G., Guswa, A. J., Celia, M. A., and Peters, C. A. (2002). Safe storage of CO₂ in deep saline aquifers. *Environ. Sci. Technol.* **36**, 240A-245A.
- Cahill, A. G., Jakobsen, R., Mathiesen, T. B., and 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**, 117-125.
- Celia, M. A., and Nordbotten, J. M. (2009). Practical modeling approaches for geological storage of carbon dioxide. *Ground Water* **47**, 627-638.
- Damen, K., Faaij, A., van Bergen, F., Gale, J., and Lysen, E. (2005). Identification of early opportunities for CO₂ sequestration-worldwide screening for CO₂-EOR and CO₂-ECBM projects. *Energy* **30**, 1931-1952.
- de Caritat, P., Hortle, A., Raistrick, M., Stalvies, C., and 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**, 16-32.
- Frye, E., Bao, C., Li, L., and Blumsack, S. (2012). Environmental Controls of Cadmium Desorption during CO₂ Leakage. *Environmental Science & Technology* **46**, 4388-4395.
- Goldberg, S., Forster, H. S., and Godfrey, C. L. (1996). Molybdenum adsorption on oxides, clay minerals, and soils. *Soil Science Society of America Journal* **60**, 425-432.
- Harvey, O. R., Qafoku, N. P., Cantrell, K. J., Lee, G., Amonette, G. E., and Brown, C. F. (2013). Geochemical Implications of Gas Leakage associated with Geologic CO₂ Storage-A Qualitative Review. *Environ. Sci. Technol.* **47**, 23-26.
- Holloway, S., Pearce, J. M., Hards, V. L., Ohsumi, T., and Gale, J. (2007). Natural emissions of CO₂ from the geosphere and their bearing on the geological storage of carbon dioxide. *Energy* **32**, 1194-1201.
- Humez, P., Lagneau, V., Lions, J., and 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.

- IPCC (2005). Special Report on Carbon Dioxide Capture and Storage Working Group III of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York.
- Jacquemet, N., Pironon, J., and Caroli, E. (2005). New Experimental Procedure for Simulation of H₂S + CO₂ Geological Storage. Application to Well Cement Aging. *Oil Gas Sci. Technol.* **60**, 193-206.
- Jordan, P., and 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**, 1103-1123.
- Keating, H. E., Fessenden, J., Kanjorski, N., Koning, D. J., and 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**, 521-536.
- Kharaka, Y. K., Thordsen, J. J., Kakouros, E., Ambats, G., Herkelrather, W. N., Beers, S. R., Birkholzer, J. T., Apps, J. A., Spycher, N. F., Zheng, L., Trautz, R. C., Rauch, H. W., and Gullickson, K. S. (2010). 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., and McCray, J. E. (2014). Metal Release from Sandstones under Experimentally and Numerically Simulated CO₂ Leakage Conditions. *Environmental Science & Technology* **48**, 1436-1442.
- Lewicki, J. L., Birkholzer, J., and 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**, 457-467.
- Little, M. G., and Jackson, R. B. (2010). Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers. *Environ. Sci. Technol.* **44**, 9225-9232.
- Lu, J., Partin, J. W., Hovorka, S. D., and Wong, C. (2010). Potential risks to freshwater resources as a result of leakage from CO₂ geological storage: a batch-reaction experiment. *Environ. Earth Sci.* **60**, 335-348.
- Metz, B., Davidson, O., de Coninck, H., Loos, M., and Meyer, L. (2005). "Carbon Dioxide Capture and Storage-Special Report of the Intergovernmental Panel on Climate Change." Cambridge University Press, Cambridge.
- Mickler, P. J., Yang, C., Scanlon, B. R., Reedy, R., and Lu, J. (2013). Potential Impacts of CO₂ Leakage on Groundwater Chemistry from Laboratory Batch Experiments and Field Push-pull Tests. *Environmental Science & Technology* **47**, 10694-10702.
- Montes-Hernandez, G., Renard, F., and 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**, 6247-6253.
- Navarre-Sitchler, A. K., Maxwell, R. M., Siirila, E. R., Hammond, G. E., and 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.
- Nisi, B., Vaselli, O., Tassi, F., de Elio, J., Huertas, A. D., Mazadiego, L. F., and Ortega, M. F. (2013). Hydrogeochemistry of surface and spring waters in the surroundings of the CO₂ injection site at Hontomin-Huermeces (Burgos, Spain). *International Journal of Greenhouse Gas Control* **14**, 151-168.
- Nordbotten, J. M., Celia, M. A., Bachu, S., and Dahle, H. K. (2005). Semianalytical solution for CO₂ leakage through an abandoned well. *Environ. Sci. Technol.* **39**, 602-611.
- Peter, A., Lamert, H., Beyer, M., Hornbruch, G., Heinrich, B., Schulz, A., Geistlinger, H., Schreiber, B., Dietrich, P., Werban, U., Vogt, C., Richnow, H. H., Grossmann, J., and Dahmke, A. (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**, 335-349.
- Qafoku, N., Brown, C., Wang, G., Sullivan, E., Lawter, A., Harvey, O., and Bowden, M. (2013). "Geochemical Impacts of Leaking CO₂ from Subsurface Storage Reservoirs to Unconfined and Confined Aquifers," Rep. No. PNNL-22420. Pacific Northwest National Laboratory.
- Qafoku, N. P., Dresel, E. P., Ilton, E., Mckinley, J. P., and Resch, C. T. (2010). Chromium(VI) transport in an acidic waste contaminated subsurface medium: The role of reduction *Chemosphere* **81**, 1492-1500.
- Qafoku, N. P., Lawter, A. R., Shao, H., Wang, G., and Brown, C. F. (2014). Evaluating Impacts of CO₂ Gas Intrusion Into a Confined Sandstone aquifer: Experimental Results. *Energy Procedia* **63**, 3275-3284.
- Romanak, K. D., Smyth, R. C., Yang, C., Hovorka, S. D., Rearick, M., and Lu, J. (2012). Sensitivity of groundwater systems to CO₂: Application of a site-specific analysis of carbonate monitoring parameters at the SACROC CO₂-enhanced oil field. *International Journal of Greenhouse Gas Control* **6**, 142-152.
- Scherer, G. W., Kutcho, B., Thaulow, N., Duguid, A., and Mook, B. (2011). Characterization of cement from a well at Teapot Dome Oil Field: Implications for geological sequestration. *Int. J. Greenhouse Gas Control* **5**, 115-124.
- Skinner, L. (2003). "CO₂ blowouts: An emerging problem : Well control and intervention," Gulf, Houston, TX, ETATS-UNIS.
- Smedley, P. L., Cooper, D. M., Ander, E. L., Milne, C. J., and Lapworth, D. J. (2014). Occurrence of molybdenum in British surface water and groundwater: Distributions, controls and implications for water supply. *Applied Geochemistry* **40**, 144-154.
- Smyth, R. C., Hovorka, S. D., Lu, J., Romanak, K. D., Partin, J. W., Wong, C., and Yang, C. (2009). Assessing risk to fresh water resources from long term CO₂ injection-laboratory and field studies. *Energy Procedia* **1**, 1957-1964.
- Trautz, R. C., Pugh, J. D., Varadharajan, C., Zheng, L. G., Bianchi, M., Nico, P. S., Spycher, N. F., Newell, D. L., Esposito, R. A., Wu, Y. X., Dafflon, B., Hubbard, S. S., and Birkholzer, J. T. (2013). Effect of Dissolved CO₂ on a Shallow Groundwater System: A Controlled Release Field Experiment. *Environmental Science & Technology* **47**, 298-305.
- U.S.EPA (2009). Code of Federal Regulations. In "40 CFR Part 141 and 143" (EPA816-F-09-0004, ed.). U.S. Environmental Protection Agency, Washington, D.C.
- Vong, C. Q., Jacquement, N., Picot-Colbeaux, G., Lions, J., Rohmer, J., and Bouc, O. (2011). Reactive transport modeling for impact assessment of a CO₂ intrusion on trace elements mobility within fresh groundwater and its natural attenuation for potential remediation. *Energy Procedia* **4**, 3171-3178.
- Wang, G., Qafoku, N., Lawter, A., Bowden, M., Harvey, O., Sullivan, C., and Brown, C. (2014). Geochemical Impacts of Leaking CO₂ from Substorage Reservoirs to an Unconfined Aquifer. *submitted*.
- Wang, S., and 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**, 2833-2848.
- Wei, Y., Maroto-Valer, M., and Steven, M. D. (2011). Environmental consequences of potential leaks of CO₂ in soil. *Energy Procedia* **4**, 3224-3230.
- Wilkin, R. T., and 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.

- Zheng, L., Apps, J. A., Zhang, Y., Xu, T., and Birkholzer, J. T. (2009). On mobilization of lead and arsenic in groundwater in response to CO₂ leakage from deep geological storage. *Chemical Geology* **268**, 281-297.
- Zheng, L., Qafoku, N., Wang, G., Shao, H., Lawter, A., and Brown, C. (2014). Evaluating and Predicting Impacts of CO₂ Intrusion into an Unconsolidated Aquifer: 2. Modeling Data. *submitted*.
- Zheng, L. G., Apps, J. A., Spycher, N., Birkholzer, J. T., Kharaka, Y. K., Thordsen, J., Beers, S. R., Herkelrath, W. N., Kakouros, E., and Trautz, R. C. (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.

Tables and figures for KS experimental manuscript (IJGGC00608)

Table 1. 8M Nitric Acid Extraction Results for CNG Sediments

UNITS		CNG 8 <2mm		CNG 60 <2mm		CNG 110 <2mm		CNG 150 <2mm	
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Aluminum	µg/g	6.48E+03	9.19E+01	2.48E+03	2.12E+01	2.22E+03	8.63E+02	2.25E+03	9.33E+02
Arsenic	µg/g	2.16E+00	1.06E-01	1.59E+00	1.56E-01	9.64E-01	5.66E-03	1.06E+00	2.83E-02
Barium	µg/g	1.73E+02	4.24E+00	2.37E+01		6.74E+01		6.45E+01	
Cadmium	µg/g	1.71E-01	1.13E-02	ND		ND		ND	
Calcium	µg/g	1.95E+04	4.24E+02	2.26E+03	3.54E+01	9.42E+03	4.36E+03	9.49E+03	4.40E+03
Cesium	µg/g	1.16E+00	3.54E-02	3.48E-01	2.62E-02	3.19E-01	7.78E-03	3.67E-01	2.12E-02
Chromium	µg/g	7.08E+00	2.69E-01	3.21E+00	3.46E-01	2.68E+00	7.07E-03	4.63E+00	2.19E-01
Iron	µg/g	8.15E+03	5.66E+01	4.36E+03	4.95E+01	3.32E+03	1.09E+03	3.36E+03	1.15E+03
Lead	µg/g	6.27E+00	2.55E-01	2.38E+00	2.40E-01	1.49E+00	2.83E-02	2.27E+00	1.20E-01
Magnesium	µg/g	3.89E+03	4.24E+01	8.33E+02	1.20E+01	1.23E+03	5.79E+02	1.23E+03	6.05E+02
Manganese	µg/g	2.22E+02	2.83E+00	4.49E+01	9.19E-01	8.86E+01	6.28E+01	8.93E+01	6.32E+01
Phosphorus	µg/g	3.72E+02	2.12E+00	5.07E+02	1.13E+01	1.62E+02	4.74E+01	1.67E+02	5.16E+01
Potassium	µg/g	1.55E+03	2.12E+01	6.79E+02	3.54E+00	4.13E+02	1.22E+02	4.17E+02	1.17E+02
Strontium	µg/g	5.96E+01	7.07E-01	ND		2.49E+01		2.52E+01	
Zinc	µg/g	2.82E+01	5.66E-01	ND		ND		ND	

Figure 1. SEM and EDS for sediments CNG 8 (a), CNG 60 (b), and CNG 150 (c).

Figure 2. Batch experiment pH change as a function of time for the four High Plains sediments used in this study. Closed symbols represent samples that received CO₂ gas and corresponding open symbols represent the samples that did not receive CO₂ gas.

Figure 3. Changes in Ca concentration as a function of time for the four High Plains sediments used in this study. Closed symbols represent samples that received CO₂ gas and corresponding open symbols represent the samples that did not receive CO₂ gas.

Figure 4. Changes in Si concentration as a function of time for the four High Plains sediments used in this study. Closed symbols represent samples that received CO₂ gas and corresponding open symbols represent the samples that did not receive CO₂ gas.

Figure 5. Changes in Mo, Mn, and Ba concentration as a function of time for the four High Plains sediments used in this study. Closed symbols represent samples that received CO₂ gas and corresponding open symbols represent the samples that did not receive CO₂ gas. CNG 60 Mn data is not included because concentrations were mostly below detection limits throughout the experiment. Orange lines and/or text represent the EPA MCL. Green lines and/or text represent the background concentration (Mo_{GW} = 0.0 µg/L, Mn_{GW} = 0.0 µg/L, Ba_{GW} = 0.0 µg/L). Dashed lines represent the detection limit for each element.

Figure 6. Changes in P (left) and As (right) concentration as a function of time in sediment sample CNG 60.

Figure 7. Column experiment results for pH and select major elements (Ca, Mg, Si) for CNG 60 (red) and CNG 110 (black). The EQL (the black dashed lines) indicates the equipment detection limit times the dilution factor. All non-zero concentrations below the EQL line should be considered as non-detect.

Figure 8. Column experiment results for select elements (Mo, Mn, As, Cs, Pb, Hg, Ba, and Ag) for CNG 60 (red) and CNG 110 (black). EPA MCLs (or EPA TTs) are indicated, when available, by orange dashed lines and/or text. The EQL (the black dashed lines) indicates the equipment detection limit times the dilution factor. All non-zero concentrations below the EQL line should be considered as non-detect.

*EPA TT indicates a level at which a treatment technique must be used to reduce the level of a contaminant