Review of the Impacts of Leaking CO$_2$ Gas and Brine on Groundwater Quality

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Abstract

This paper provides an overview of the existing data and knowledge presented in recent literature about the potential leaking of CO_2 from the deep subsurface storage reservoirs and the effects on groundwater quality. The objectives are to: 1) present data and discuss potential risks associated with the groundwater quality degradation due to CO_2 gas and brine exposure; 2) identify the set of geochemical data required to develop models to assess and predict aquifer responses to CO_2 and brine leakage; and 3) present a summary of the findings and reveal future trends in this important and expanding research area. The discussion is focused around aquifer responses to CO_2 gas and brine exposure and the degree of impact; major hydrogeological and geochemical processes and site-specific properties known to control aquifer quality under CO_2 exposure conditions; contributions from the deep reservoirs (plume characteristics and composition); and the possibility of establishment of a new network of reactions and processes affecting or controlling the overall mobility of major, minor, and trace elements and the fate of the elements released from sediments or transported with brine. This paper also includes a discussion on the development of conceptual and reduced order models (ROMs) to describe and predict aquifer responses and whether or not the release of metals following exposure to CO_2 is harmful, which are an essential tool for CO_2 sequestration related risk assessment. Future research needs in this area are also included at the end of the paper.

Keywords: CO_2 sequestration; CO_2 subsurface storage; groundwater quality; aquifers; reservoir brine; reservoir contaminants; groundwater; CO_2-induced mineral dissolution; aquifer contaminants.

Content

1.0   Introduction

Geological carbon sequestration (GCS) is a global carbon emission reduction strategy involving the capture of CO_2 emitted from fossil fuel burning power plants, as well as the subsequent injection of the captured CO_2 gas into deep saline aquifers or depleted oil and gas reservoirs. A critical question that arises from the proposed GCS is the potential impacts of CO_2 injection on the quality of drinking-water systems overlying CO_2 sequestration storage sites.

Although storage reservoirs are evaluated and selected based on their ability to safely and securely store emplaced fluids, leakage of CO_2 from storage reservoirs is a primary risk factor and potential barrier to the widespread acceptance of geologic CO_2 sequestration (DOE, 2007; Harvey et al., 2013; Jun et al., 2013). Therefore, a systematic understanding of how CO_2 leakage would affect the geochemistry of potable aquifers, and subsequently control or affect elemental and contaminant release via sequential and/or simultaneous abiotic and biotic processes and reactions is vital.

Two possible scenarios for CO_2 leakage have been identified in recent publications: a sudden, fast, and short-lived release of CO_2, as seen in the case of a well failure during injection or a sudden blowout (Holloway, 2007; Jordan, 2009; Skinner, 2003), or a slower, more gradual leak, 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; Xiao et al., 2016). However, well related leaks appear to be declining thanks to improved construction and operation (Newmark et al., 2010).

This review paper provides a broad view of the existing knowledge and summarizes data and findings that have been published in the literature over the last several years in this important topical area. The objectives of this paper are to: 1) present and discuss potential risks for groundwater degradation due to CO_2 gas and brine exposure; 2) identify the set of geochemical data required to assess and predict aquifer responses to CO_2 and brine leakage; and 3) present a summary of the findings and reveal future trends in this important and expanding research area. Specifically, the paper is focused on: i.) aquifer responses

such as changes in aqueous phase/groundwater pH and chemical composition as a result of exposure to the leaking CO_2 gas; ii.) major site-specific properties such as solid phase chemistry and mineralogy and contributions from the deep storage reservoirs to groundwater quality; iii.) the possibility of the establishment of a new network of reactions and processes affecting or controlling overall mobility of major, minor, and trace elements released from aquifer rocks or sediments and/or those traveling upwards from the storage reservoirs; and iv.) development of conceptual and reduced order models (ROMs) to describe and predict significant and/or insignificant site-specific aquifer responses. The readers are also referred to previous review papers that have delved partially or fully into this subject: Harvey et al. (2013) thoroughly discussed early results and potential deleterious and/or beneficial effects of CO_2 in aquifer systems, and Jones et al. (2015), in which a broader view of potential impacts is discussed, including both onshore and offshore ecosystems.

2.0   Potential Risk to Groundwater Due to CO_2 Gas and Brine Intrusion

2.1   General overview

Upon entering an aquifer, a portion of the CO_2 gas will dissolve into the groundwater, which will cause a subsequent decrease in aqueous pH (Trautz et al., 2013) due to the formation and disassociation of carbonic acid (Harvey et al., 2013). The reduced pH can then cause an increase in the mobilization of major (Ca, Mg, K, Na, etc) and minor (Fe, Al, Ba, etc.) elements as well as potential contaminants (As, Pb, Cd, etc.) via desorption and/or dissolution reactions. Changes in other water quality parameters, such as alkalinity, salinity, and total dissolved solids (TDS) may also occur. Brine can also be brought upward into an overlying groundwater aquifer with increased pressure due to CO_2 injection (Oldenburg and Rinaldi, 2011). Salinity of the brine, as well as presence of contaminants, such as As and Cd, can vary and can increase negative effects on the aquifer.

Over the last decade, a number of studies have been undertaken to assess the impacts of potential CO_2 leakage from deep storage reservoirs on the quality of overlying freshwater aquifers. These studies include natural analogs (Caritat et al., 2013; Keating et al., 2010; Lewicki et al., 2007), field in-situ CO_2 injections (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., 2016; Wei et al., 2011).

However, the results of the studies are inconsistent and, in some cases, contradictory as some indicate CO_2 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), some indicate low levels of risk (Frye et al., 2012; Keating et al., 2010; Kirsch et al., 2014; Mickler et al., 2013), and others have found some possible benefits (such as the removal of As, U, V, and Cr) related to CO_2 leakage into groundwater (Lu et al., 2010; Smyth et al., 2009). Clearly, the scientific community has not yet reached an agreement on the important issue of deciding whether the impacts from the leakage of CO_2 into groundwater are negative, insignificant, or positive.

In an attempt to gain further insights on this important subject, we initially analyzed the results of a variety of modeling efforts and laboratory and field studies conducted in different sites and aquifers within the U.S. (Table 1). Because site-specific properties, such as solid phase chemical, physical and mineralogical properties play a critical role on how the aquifer system reacts to CO_2 gas and brine intrusion, it is important to consider different types of aquifers in this analysis.

Table 1. Select recent studies conducted in different sites and types of aquifers.

Project Site	Paper	Major Details/Results
ZERT- Bozeman, MT (field study)	Kharaka et al. (2010)	Water samples from the site were analyzed before, during, and after injection of CO_2 1-2 m below the water table for 30 days. Rapid and systematic changes were observed in pH, alkalinity and EC; CO_2 caused increases in Ca, Mg, Fe, Mn, BTEX, and other metals and a lower pH, , but all were significantly below (above for pH) maximum

Project Site	Paper	Major Details/Results
		concentration limits (MCL).
	Apps et al. (2011); Zheng et al. (2012)	A geochemical model was used to simulate processes likely to be responsible for dissolved constituents found in the water samples from the site. Model results suggested that dissolved CO_2 induced calcite dissolution, Ca-driven cation exchange reactions caused increased trace metal concentrations, and competition for sorption sites may have driven increased As and Se levels.
High Plains: an unconsolidated sand and gravel aquifer		
Ogallala aquifer, TX (Southern High Plains)	Little and Jackson (2010)	Lab experiments were conducted to compare metal release from aquifer materials from MD, VA and IL; Al, Mn, Fe, Zn, Cd, Se, Ba, Tl, and U approached or exceeded MCL's.
	Xiao et al. (2016)	Geochemical simulations were used to determine likely leakage rates from likely leakage pathways and permeabilities. Worst-case scenarios indicate low levels of trace metal release, with concentrations in the aquifer remaining below no-impact thresholds.
Central High Plains	Carroll et al. (2014b)	Model simulations of CO_2 leakage were used to predict plume size, potential impacts, detection, time scale, and "no-impact" thresholds.
	Lawter et al. (2015)	Laboratory batch and column studies using 1% CH_4 and As/Cd spiked SGW concluded that the addition of 1% CH_4 is unlikely to change pH or increase contaminant release from aquifer materials.
	Lawter et al. (2015b)	These batch and column experiments used an As/Cd spiked synthetic groundwater (SGW) to represent possible contaminants originating from reservoir brine and being transported into an overlying aquifer with leaking CO_2. Results indicated that the adsorption capacity of the High Plains material was able remove most or all of the As and Cd from the liquid phase.
	Lawter et al. (2016)	Batch and column experiments were conducted to determine the maximum expected elemental concentrations released from sediments following CO_2 intrusion. These results were used to feed into the modeling experiment conducted by Zheng et al. (2016).
	Zheng et al. (2016)	Modeling experiments were conducted to determine the likely processes controlling geochemical changes observed in Lawter et al. (2016). Results indicated that calcite content, CEC and adsorption capacity were important drivers of increased elemental concentrations.
Chimayo, NM- natural	Keating et al. (2010)	This natural analog study found that high levels of CO_2 did not have a major effect on pH or trace

Project Site	Paper	Major Details/Results
analog site (field study)		metal mobility due to buffering by the aquifer. In wells with brakish waters carrying the CO_2 upward, however, significant levels of contaminants were also brought upward (e.g., As, U, and Pb).
	Viswanathan et al. (2012)	The Chimayo site has elevated As levels [above U.S. Environmental Protection Agency (EPA) MCLs]. Modeling and batch experiments were conducted to determine the source of As and the mechanism for decreased concentrations over time in the batch experiments. Results indicated that sorption onto clays and precipitation of kaolinite during the experiment caused the slow decrease in As.
	Keating et al. (2013a)	Field and experimental results indicate that most U found in the natural analog site was from brackish waters, and not from CO_2-induced calcite dissolution. A 3-D reactive transport model was used to capture the essential geochemical reactions that control CO_2/aquifer interactions at the site; results indicated that if a leak is short in duration, CO_2-induced U mobilization will be minor but persistent.
	Keating et al. (2013b)	This study compared to Chimayo, NM to Springerville, AZ; both are natural analog sites where CO_2 leaks through brine but salinity is not increased in Springerville; in Chimayo, salinity is significantly increased. Multiphase transport simulations were used to show small fault zones may increase likeliness of brine displacement while wide fault zones may allow CO_2 mobility without co-transportation of brine.
Springerville, AZ (natural analog site)	Keating et al. (2014b)	This paper found dissolved CO_2 upward movement was greater than buoyant free gas movement.
SACROC- 35 year CO_2 enhanced oil recovery site sitting under Dockum aquifer in TX (sandstone and conglomerate)	Smyth et al. (2009)	Laboratory batch experiments were conducted to determine the effect of injected CO_2 on mobilization of elements from the host rock. Field studies were then conducted to determine if the long-term injection of CO_2 for EOR had a negative effect on the groundwater, using lab-determined indicators, but no degradation of water sources was found.
	Romanak et al. (2012)	Geochemical characterization of Dockum aquifer was followed by a hypothetical leakage model. Results indicated that usefulness of many monitoring parameters will vary by site, but use of DIC could be used to monitor at a variety of sites.
Edwards Aquifer, TX- carbonate aquifer	Qafoku et al. (2013)	This report covers numerous Edwards and High Plains batch and column studies conducted during or before 2013.
	Carroll et al. (2014b)	Model simulations of CO_2 leakage was used to predict plume size, potential impacts, detection,

Project Site	Paper	Major Details/Results
		time scale, and "no-impact" thresholds.
	Bacon et al. (2016)	Modeling of the results from the batch and column studies presented in the paper by Wang et al. (2016)
	Dai et al. (2014)	Following Monte Carlo simulations, five risk proxies were chosen for probability distribution analysis. Changes in pH, TDS, and trace concentrations of As, Cd, and Pb were included, and analysis of the controlling aquifer characteristics for each risk proxy was determined.
	Wang et al. (2016)	Results of batch and column studies using Edwards aquifer material found rapid mobilization of major and minor elements. Trace metals were released in low but sustained concentrations.
Plant Daniel, MS (EPRI site)- Field-scale controlled release of CO_2 into a shallow groundwater formation Plant Daniel Power plant	Trautz et al. (2013)	Groundwater sampling after injection of CO_2 showed a decrease in pH (~3 units) but pulse-like behavior for alkalinity and conductivity. No inorganics regulated by the EPA exceeded MCLs during testing. A reactive transport model was then tested using the obtained data, with good agreement for pH, Ca, Mg, K, and Sr, and lesser agreement for Mn, Ba, Cr, and Fe.
	Varadharajan et al. (2013)	Sediment characterization of the Plant Daniel site was combined with laboratory studies to compare results with field studies and determine the cause of elemental changes. Most elemental release was pH-driven; the study concluded that pH and certain indicator cations (e.g., Na, Ba, Ca) could be used for monitoring.
Cranfield, MS (SECARB)- CO_2 injection into a depleted gas and oil reservoir	Yang et al. (2013)	A push-pull test was conducted to determine the effect of CO_2 on the aquifer. Results indicated that trace element concentrations increased after injection of CO_2-enriched groundwater, but remained below MCLs.

This assortment of studies assessed the conditions that cause CO_2 leaking in a variety of sites, estimated risks related to CO_2 leakage from wells and reservoirs, and proposed monitoring techniques. In addition, and more importantly, these studies provided a good estimation of the CO_2 leakage effects on the quality of groundwater and aquifers, assessed important risk factors to groundwater quality, and some modeling simulations were successful at predicting plume size, potential impacts, detection, time scale,

and "no-impact" thresholds. On the other side, these studies clearly showed the site (and experimental protocol) specific nature of the results which make them difficult to compare.

The following subsections of the paper includes an in-depth look at the effects of short and long term CO_2 gas exposure on TDS and pH and potential inorganic and organic contaminant release from aquifer rocks and sediments into the aqueous phase and their subsequent fate. Subject to this investigative effort are two representative aquifer types that commonly overlie potential CO_2 sequestration reservoirs: unconfined limestone aquifers (e.g., the Edwards aquifer in TX), and unconsolidated sand and gravel aquifers (e.g., the High Plains aquifer in KS). Results from other sites and aquifers are included and discussed as well.

2.2 Controls over pH and TDS

Previous studies have investigated the CO_2 gas induced decrease in the groundwater pH and the properties, processes, reactions and parameters that control the pH drop. A study conducted with a variety of sediments from the High Plains aquifer revealed important mineralogy related differences in the pH (Lawter et al., 2016). All sediments, except one, had XRD detectable amounts of calcite. After exposure to CO_2 gas, the pH of the calcite-containing sediments decreased from neutral to ~ 6, while the pH of the calcite-free sediment decreased to ~5, mainly due to the smaller buffering capacity of the latter sediment. More importantly, the aqueous phase of the calcite-free sediment had greater concentrations of elements released from the solid phase including potential contaminants. In another study conducted with rocks and weathered rocks from the unconfined portion of the Edwards aquifer exposed to CO_2-rich synthetic groundwater (Wang et al., 2016), the effect on pH was similar in all tested materials (the pH did not decrease below ~ 6), due to the high calcite content and buffering capacity of the sediments. Other experiments conducted with limestone and dolomite samples produced very similar results; the pH decreased from an initial value of 9.5 to <6.5 in the limestone study and <5.6 in the dolomite study (Wunsch et al., 2014; Wunsch et al., 2013). These examples demonstrate the role of mineralogy as a major control over pH change.

A reactive transport modeling study described and interpreted the observed aqueous elemental concentration changes in a series of column experiments conducted with the High Plains aquifer sediment, attempting to shed additional light on key chemical reactions and parameters controlling aqueous pH, TDS and elemental concentration changes (Zheng et al., 2016). The initial geochemical conceptual model was similar to the conceptual models previously developed using data from two field tests: the Montana State University-Zero Emissions Research and Technology (MSU-ZERT) field test in Montana (Kharaka et al., 2010; Zheng et al., 2012), and a field test conducted in Plant Daniel, Mississippi (Trautz et al., 2013). Both of these tests were conducted on a sandstone aquifer, with a similar mineralogy to that of the High Plains aquifer. Due to these similarities between the aquifers, the geochemical conceptual model developed based on data from the field tests was capable of predicting responses of the High Plains aquifer materials (Zheng et al., 2016). This study found that the dissolution of calcite was the primary pH buffering process, with the dissolution of magnesite and surface protonation playing secondary roles. A somewhat different conceptual model was developed for the unconfined portion of the Edwards aquifer in Texas with a mineralogy consisting almost entirely of calcite (Wang et al., 2016), with a small amount of dolomite (Maclay and Small, 1994) and a minor amount of strontianite included in the calcite crystal structure (Tesoriero and Pankow, 1996) (Table 2).

Table 2. Mineral reactions included in the Edwards aquifer conceptual model (Bacon et al., 2016)

Kinetic Reaction	Equilibrium Coefficient at 25°C, log	Forward Rate at 25°C, mol/m²/s	Activation Energy, kJ/mol
$Calcite + H^+ = HCO_3^- + Ca^{+2}$	1.847	1.5e-6	23.5
$Dolomite + 2H^+ = 2HCO_3^- + Ca^{+2} + Mg^{+2}$	3.533	2.9e-8	52.2

Strontianite $= CO_3^- + Sr^{+2}$ -9.271   Same as calcite   Same as calcite

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For the column experiments conducted with unweathered rock samples, calcite and dolomite were included in the model, and adjustments were made for the amount of strontium in solid solution with calcite (Bacon et al., 2016). The concentration of dissolved CO_2 in the inlet water was adjusted to match the observed pH, which decreased to ~6.5. TDS was calculated based on measured major ion concentrations and increased from a value of 161 mg/L at the beginning to a value of 353 mg/L at the end of the column experiment. The reported median value of TDS in the urban, unconfined portion of the Edwards aquifer is 329 mg/L (Musgrove et al., 2010). The experimentally observed TDS was lower than the reported 75th percentile value of 360 mg/L. The modeling approaches described above were successful in portraying and predicting aquifer response in terms of pH and TDS changes should CO_2-brine solutions travel from deep subsurface storage reservoirs into the aquifers.

Not many studies have looked at the effect of leaking CO_2 saturated saline brines on aquifer pH, and the ability of these brines to significantly alter solution pH is not well explored. This may be important, particularly in aquifers with low buffering capacities. Another important aspect was emphasized in a recent study that showed that the solubility of CO_2 was decreased in high saline solutions; this and the resulting decrease in carbonic acid formed may prevent a significant decrease in aqueous pH (Horner et al., 2015), thereby affecting and/or controlling the rate and extent of pH-dependent reactions in aquifers.

2.3 Controls over contaminant release (Inorganic and Organic)

In this section data from research efforts conducted with samples from sandstone or sand/gravel, carbonate and other aquifers, is analyzed to determine important properties, processes, reactions and parameters that control contaminant release to the aqueous phase when these subsurface systems are exposed to excess CO_2.

2.3.1. Sandstone and sand/gravel aquifers

Column experiments conducted with High Plains aquifer sediments showed that the effluent water had significant concentrations of major elements (e.g., Si, Ca, Mg, Na, K), minor elements (e.g., Al, Fe, Mn), and trace elements (e.g., Sb, Sr, Ba, Cr, Se, As, Pb, Cs, Cu, and Zn) (Lawter et al., 2016). Reactive transport modeling suggested that calcite dissolution and Ca-driven cation exchange were responsible for the release of Ca, Mg, Na, K, Sr, Cs, and Ba, and adsorption/desorption reactions controlled the release of As (Fig. 1) and Pb.
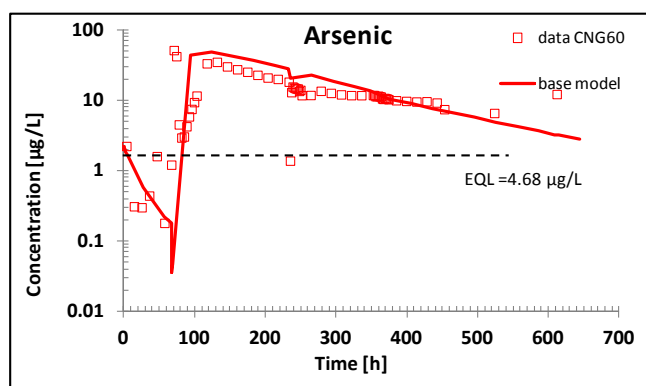

Figure 1. Simulated and observed breakthrough curves of As, High Plains sediment (Zheng et al., 2016).

Model interpretation of the column tests also helped to constrain key parameters such as calcite volume fraction, cation exchange capacity (CEC), and the volume fraction of adsorbent (goethite). A volume fraction of calcite below the XRD detection limit was used in the model for the field test described in Trautz et al. (2013), where the presence of calcite in the sediments was later confirmed by micro-X ray spectroscopy. This limited amount of calcite that would be depleted after the intrusion of CO_2 was key to reproducing the pulse-like breakthrough curve of the concentration of alkali and alkaline earth metals in the effluent of the column test. Another parameter of contaminant (As and Pb) adsorption/desorption reactions included in the reactive transport model was the adsorption capacity (the product of the amount of adsorbent volume fraction and the surface area of the adsorbent). In the modeling simulation, the amount of adsorbent was a calibrated parameter based on the experimental data,

while the surface area of the adsorbent was fixed (40 m^2/g). These efforts clearly showed that laboratory experiments integrated with reactive transport model simulations was an efficient approach to determining key chemical reactions and parameters that control the response of an aquifer to leaking CO_2.

Studies conducted in other aquifers have reported experimental and modeling data used to conduct an evaluation of the groundwater quality changes as a result of a potential leakage of CO_2 (Altevogt and Jaffe, 2005; Apps et al., 2010; Carroll et al., 2009; Jacquemet et al., 2011; Vong et al., 2011; Wang and Jaffe, 2004; Wilkin and Digiulio, 2010; Zheng et al., 2009). Studies have also looked at the chemical reactions that control the CO_2-induced release of metals via model interpretation of laboratory experiments (Kirsch et al., 2014; Viswanathan et al., 2012; Wunsch et al., 2014) and field tests (Trautz et al., 2013; Zheng et al., 2012). In general, these models predicted the release of trace metals such as Pb and As (Apps et al., 2010; Wang and Jaffe, 2004; Zheng et al., 2009), which was largely consistent with the observations from laboratory experiments (Humez et al., 2013; Kirsch et al., 2014; Little and Jackson, 2010; Lu et al., 2010; Smyth et al., 2009; Varadharajan et al., 2013; Viswanathan et al., 2012; Wunsch et al., 2014), although the type and aqueous concentration of metal being released varied among experiments, emphasizing again the importance of the site-specific properties on the elemental release.

2.3.2. Carbonate aquifers

The results of a series of column experiments conducted with the Edwards aquifer materials were compared to the aquifer maximum concentrations and MCLs in Table 3 (Bacon et al., 2016). The hydraulically saturated column experiments were conducted in periods of continuous and stop flow events (where flow of the CO_2-rich solution was periodically stopped to determine the effect of increased residence time on elemental release). Concentrations were generally higher immediately following the stop-flow events. At the end of the first stop-flow period, for example, all of the trace metals except for Cr exceeded the maximum aquifer-observed values, and As, Pb, Sb, and Se exceeded the MCL limits. At the end of the second stop-flow period, Ba and Cr exceeded the observed aquifer maximums and only As,

Pb, and Sb exceeded the MCL. However, concentrations of the trace metals generally decreased during the continuous constant flow periods. By the last flow period, only Sb and Se exceeded the aquifer maximum threshold and no trace metals exceeded their respective MCLs.

Table 3. Summary of column experiment trace metal concentrations at the end of each experimental stage, relative to aquifer maximum concentrations and MCL regulatory limits (grey background indicates aquifer maximum exceeded, black background indicates MCL exceeded) (Bacon et al., 2016).

Experiment Stage	As	Ba	Cr	Cu	Pb	Sb	Se
Flow 1	1.00	19.5	0.590	1.52	1.32	0.690	3.01
Stop-Flow 1	44.7	203	2.03	58.2	817	17.8	150
Flow 2	0.460	10.8	0.580	1.80	0.180	0.170	1.07
Stop-Flow 2	10.1	88.2	18.1	10.9	45.0	8.64	34.5
Flow 3	0.750	5.66	0.460	0.660	0.150	0.210	2.56
Threshold	**As**	**Ba**	**Cr**	**Cu**	**Pb**	**Sb**	**Se**
Aquifer Max, µg/L	1.11	69.9	5.57	57.3	0.15	0.06	1.40
MCL, µg/L	10	2000	100	1300	15	6	50

The trend of release of the trace metals with time in the column experiments was very different than that of the major ions. Whereas the major ions increased to a stable value and showed small spikes immediately following the stop-flow events, the trace metal concentrations generally decreased with time and showed relatively large spikes following the stop-flow events (Fig. 2).
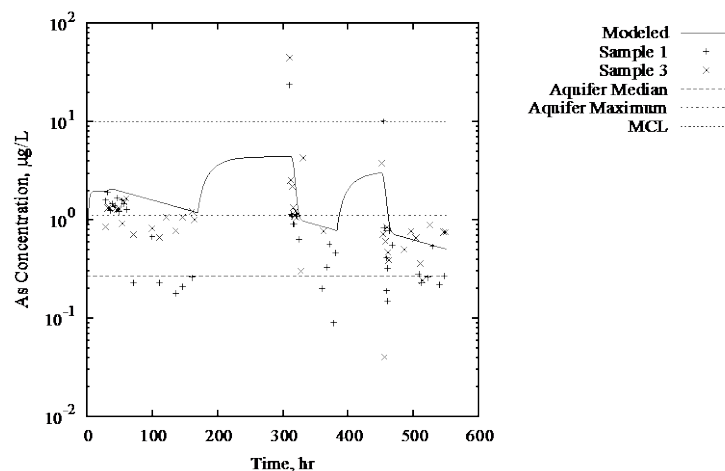
Figure 2. Arsenic modeling results compared to column experiment results and aquifer concentrations (Bacon et al., 2016).

In addition to the column experiments, a series of batch experiments was conducted with the Edwards aquifer materials. Speciation and surface complexation modeling of the batch experiments was conducted using PHREEQC (Parkhurst and Appelo, 1999) and the thermo.com.V8.R6 database (Wolery and Jarek, 2003). Modeling of the column experiments was conducted with the multiphase flow and reactive transport solver STOMP-CO$_2$-R (White et al., 2012) with ECKEChem (White and McGrail, 2005). The STOMP simulations used a smaller subset of equilibrium aqueous complexation reactions extracted from PHREEQC simulations of the batch experiments (Bacon et al., 2016) and groundwater samples (Musgrove et al., 2010) taken from the unconfined/urban portion of the Edwards aquifer (Fig. 3).
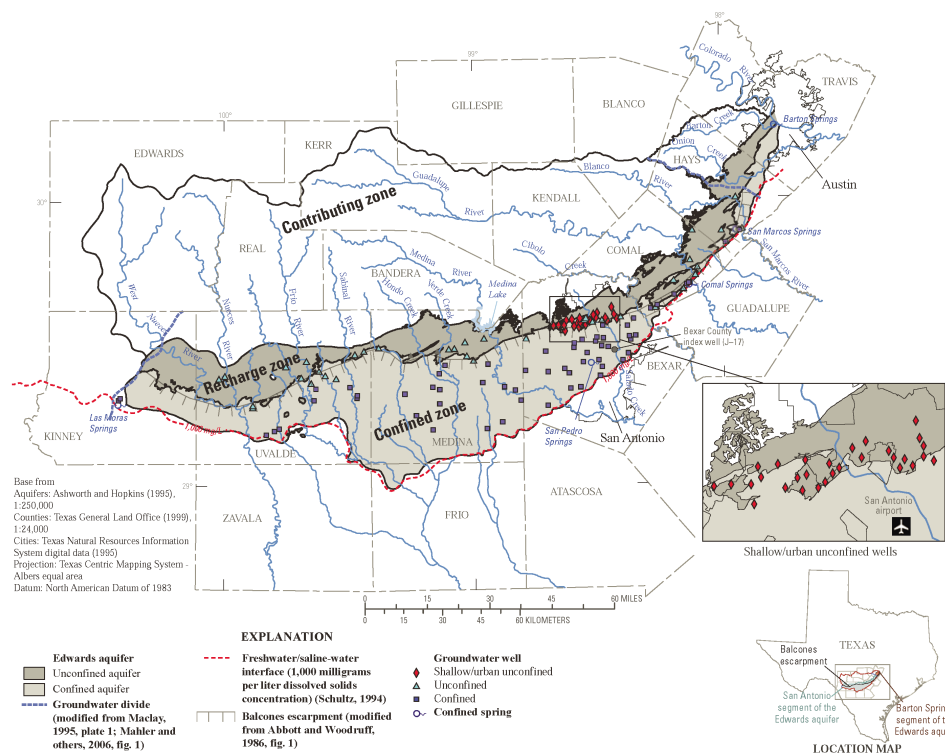
Figure 3: Map of the Edwards aquifer; the inset shows the shallow, unconfined portion of the aquifer (Musgrove et al., 2010).

According to Bacon et al. (2016), due to the limited amount of trace metals released and the high water:rock ratio in the batch experiments, the modeling of these experiments was less informative than the modeling of the column experiments. The column experiment modeling results indicated kinetic desorption as the controlling factor for release of As (Fig. 2), Ba, Cu, Cr, Pb, Se, and Sb into the liquid phase. Solid solution dissolution of calcite was the likely source of aqueous Ca, Mg, and Sr. While most elements had good fit between the model and column experiment results, some trace elements, such as Pb, did not fit well and may require a single-rate model for improved results (Bacon et al., 2016).

In a carbonate focused study, Wunsch et al. (2014) and Wunsch et al. (2013) used laboratory experiments to study metal release from limestones and dolomites, respectively. These carbonate aquifer

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materials were placed in batch reactors with a 1:5 solid to solution ratio, with pCO_2 ranging from 0.01 to 1 bar. Results of the limestone experiments showed an increase in Ca following an increase in pCO_2, then stabilizing with time. Ba, Sr, Co, and As followed the Ca trend, as did Mg in one of the limestone samples. Pb, Tl, Si, and U were also released from one or both limestone samples, but did not follow the same trend as Ca, and sulfates continually increased for the duration of the experiment. In the dolomite experiments, both Ca and Mg concentrations began to increase immediately. Concentrations of As, Ba, Co, Cs, Ge, Mn, Mo, Ni, Rb, Sb, Sr, Tl, and Zn were also elevated in at least one of the dolomite leachate samples. The two studies concluded that carbonates were the source of several contaminants found in the aqueous samples. However, many of these contaminants were removed from solution with the return to atmospheric conditions at the end of experiments. These studies showed the potential for contaminant release from carbonate aquifers, despite the potential for high buffering capacities in these aquifers (Wunsch et al., 2014; Wunsch et al., 2013).

In another study, Montes-Hernandez et al. (2013), used synthetic goethite and calcite in batch experiments. The results showed the presence of these two minerals prevented remobilization of Cu(II), Cd(II), Se(IV), and As(V), and increased adsorption of Se(IV) and As(V), although As(III) was partially remobilized with the presence of CO_2. Cahill et al. (2013) used batch experiments to study differences in water chemistry changes for chalk, calcareous sand, and siliceous sand, concluding that carbonate materials had the greatest change in chemistry but the least change in pH. According to this study, the greater change in pH in the siliceous sand represented a greater risk for mobilization of toxic elements, although lower concentrations of toxic elements released from carbonates could also present a risk to water quality. Wang and Jaffe (2004) used numerical simulations and geochemical transport modeling to predict the solubilization of trace metals, with a focus on Pb in galena-quartz and galena-calcite systems, concluding the higher alkalinity and pH of the calcite system significantly reduced the detrimental effects of the presence of CO_2. A batch experiment conducted by Lu et al. (2010) contradictorily to the conclusions of Wang and Jaffe (2004) but in agreement with Cahill et al. (2013), suggests aquifers

containing carbonate rocks are of particular concern due to the presence of Ba, Mn, and Sr in carbonates, in addition to increased alkalinity which followed carbonate dissolution.

2.3.3. Analyses of the results

Over the last decade, a number of natural analogs and field-scale in-situ CO_2 injection test sites have been subject to many recent studies as it was shown in the previous sections of this paper. In addition, laboratory-scale column and batch studies have also been conducted to determine the impacts of potential CO_2 leakage from deep storage reservoirs on the quality of overlying freshwater aquifers. The results are, on one side, consistent with one another. ***First*** the studies showed that the cause of aqueous elemental concentration change and rapid mobilization after CO_2 exposure was the significant (1-2 units), or even dramatic (about 3 units), rapid and systematic decrease in pH, which triggered a series of pH-driven chemical reactions (e.g., mineral dissolution and re-precipitation, adsorption and/or desorption, and redox transformation), and possibly, a pulse like behavior for alkalinity and conductivity. ***Second***, based on the newly-established reaction framework, reactive transport models were used to achieve good agreement for pH and major cations such as Ca, Mg, K, and Sr, but lesser agreement for minor elements such as Mn, Ba, Cr, and Fe. ***Third***, these studies demonstrated that pH and indicator cations (e.g., Na, Ba, Ca) could be used for monitoring purposes, although results also indicated that usefulness of many monitoring parameters will vary by site. Generic parameters, such as DIC could be used to monitor at a variety of sites*. ***Fourth***, modeling efforts determined the likely processes controlling geochemical changes and found that site specific properties such as mineralogy (e.g., calcite content), or other solid phase chemical properties, such as CEC and adsorption capacity were important drivers controlling aqueous elemental concentrations after aquifer CO_2 exposure. ***Fifth***, experiments conducted with gas mixtures CH_4 and CO_2 and As and Cd spiked SGW concluded that the addition of 1% CH_4 was unlikely to change pH or increase contaminant release from aquifer materials.

On the other side, some of the results presented in the literature are inconsistent and/or inconclusive. *__First__*, while most of the studies demonstrated significant changes in pH after CO_2 exposure, some of them found that high levels of CO_2 did not have a major effect on pH due to buffering by the aquifer. *__Second__*, some studies claimed that inorganic trace element concentrations regulated by the EPA increased after injection of CO_2-enriched groundwater, but they remained below MCLs. The trace elements usually occurred as impurities in mineral structures or as sorbed phases on mineral surfaces. Other studies claimed that the increase of some trace element concentrations was significant and above MCLs. A third group of studies found that trace metals were released in low but sustained concentrations contrary to other studies that found that trace element concentration decreased with time due to sorption and precipitation reactions. A fourth group of modeling studies suggested that dissolved CO_2 induced calcite dissolution, and Ca-driven cation exchange reactions increased trace metal concentrations, and competition for sorption sites increased aqueous As levels. *__Third__*, studies have shown that significant levels of contaminants may move upward (e.g., As, U, and Pb) from reservoirs together with the brine and CO_2 resulting in decreased groundwater quality. However, experiments that used an As and Cd spiked SGW to represent possible contaminants originating from reservoir brine and being transported into an overlying aquifer with leaking CO_2 showed that the adsorption capacity was able to remove most or all of the As and Cd from the liquid phase. *__Fourth__*, while each laboratory study can be viewed and evaluated on an individual basis as useful in identifying risks related to inadvertent leaks of CO_2 on an overlying groundwater aquifer, it was difficult to apply the information to a variety of aquifers because the results were not comparable between studies. Variables among experiments include differing background solution, size fraction, agitation of the batch experiments (i.e., by constant stirring or shaking), pressure, time, and solid to solution ratio. However, despite the differences in results caused by these variables, current literature suggested the most significant differences were related to the matrix of the solids being studied. *__Fifth__*, despite potential trace metal release, most current research results showed releases below the EPA MCL requirements for drinking water, resulting in a small potential risk for groundwater aquifers due to CO_2 leakage when considering current water quality regulations. However, if studies used

a "no-impact" threshold, as discussed in Section 3.1, the risk might be larger. ***Sixth,*** a comparison of the

batch and laboratory experiments revealed that Ca concentrations from batch tests using similar samples

were elevated by as much as a factor of 2.5 over column studies. This highlighted the importance of

leakage and flow rates, as the reactions that control aqueous trace metal concentrations are time

dependent (these concentrations were significantly lower during the flow portions of the column

experiments but increased after stop-flows, indicating dependency on the fluid residence time and/or pH;

pH also increased following the stop-flow events).

Importantly, release of trace metals, especially those of environmental relevance such as As, Pb, Ba,

and Cd, has not been observed in field tests (Cahill and Jakobsen, 2013; Kharaka et al., 2010; Peter et al.,

2012; Spangler et al., 2010; Trautz et al., 2013; Yang et al., 2013). Field tests have shown increased

aqueous concentrations of 20-700% compared to pre-CO_2 concentrations, but laboratory experiments

often have shown increases of several orders of magnitude (Zheng et al., 2015). Analysis of the samples

collected at the MSU-ZERT site in Bozeman, MT (Table 1) showed that although pH, alkalinity, and

several constituents changed in the groundwater during injection, none of the changes exceeded EPA

MCL's (Kharaka et al., 2010). The difference between the observation of laboratory and field tests in

terms of the release of trace metals is likely because the laboratory (especially batch) experiments are

more aggressive in leaching out trace metals due to the use of unfitting water compositions, manipulation

of the particle size of material tested, well-mixing, oxidation, high water/solid ratios, and longer reaction

time. However, release of alkali and alkaline earth metals, including Na, K, Ca, Mg, Sr, and Ba, were

commonly observed in both the laboratory and field experiments, although, again, the degree of release is

different in the laboratory and field tests.

At another site, SACROC, geochemical characterization of the Dockum aquifer was followed by a

hypothetical leakage model to show expected reactions in the aquifer due to CO_2 leakage (Romanak et al.,

2012). Romanak et al. (2012) concluded that current parameters used in leakage detection are site-

specific, but the use of dissolved inorganic carbon (DIC) as a parameter may reduce the need for site-

specific parameters, as they found the DIC response to be similar across many modeled environments. Laboratory batch studies indicated several constituents would increase and pH would decrease if CO_2 were to leak into the overlying Dockum aquifer. However, a field study of several wells located inside and outside the SACROC oil field showed no degradation of groundwater resources due to CO_2 injection. While some elemental concentrations exceeded EPA MCLs, this occurred more outside the SACROC area than inside the oil field (Smyth et al., 2009).

2.4   Major site-specific properties that control groundwater quality

The following section provides an in-depth discussion about three important site-specific properties: mineralogy, solid phase chemistry and contributions to aquifer contamination from deep subsurface reservoirs. Additional evidence on how these site-specific properties can play an important role in controlling groundwater quality and the way an aquifer would respond to the exposure of leaking CO_2 (and other gases) and brine from the deep subsurface reservoirs, is also presented.

2.4.1   Mineralogy and solid phase chemistry

The importance of mineralogy (and especially calcite content) in the sediment is clearly stated in recent studies (Cahill and Jakobsen, 2013; Frye et al., 2012; Keating et al., 2010; Little and Jackson, 2010; Lu et al., 2010; Wunsch et al., 2014; Wunsch et al., 2013). On one side, calcite (and other carbonate minerals) may buffer the pH of the aquifer against further pH change (Cahill et al., 2013; Little and Jackson, 2010), decreasing the extent of the dissolution of other minerals resulting in a smaller release of potential contaminants, as noted in the High Plains experiments and other studies (e.g., Frye et al. (2012)), and controlling the extent and rate of pH dependent reactions. Calcite is the predominant mineral in carbonate aquifers, although fewer studies have been conducted with the carbonate aquifers despite their prevalence as sources of potable water overlying potential sequestration reservoirs within the continental U.S (Fig. 4). Weathered samples, however, may contain other minerals in addition to calcite; e.g., some samples from the Edwards aquifer had XRD detectable amounts of quartz, phyllosilicates and

montmorillonite (Wang et al., 2016). The literature includes several other studies with variable carbonate content where carbonate minerals are present but the aquifer is not dominated by carbonates (Cahill et al., 2013; Montes-Hernandez et al., 2013; Wang and Jaffe, 2004).
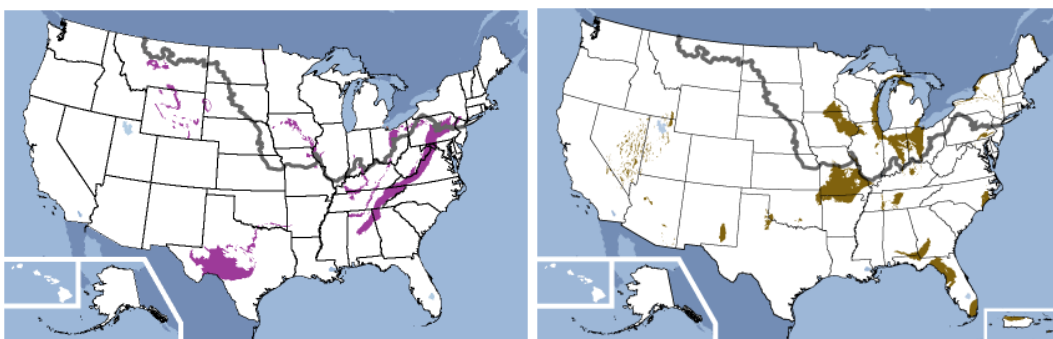

Figure 4. Locations of sand/carbonate (left, violet) and carbonate (right, brown) shallow drinking waters (http://water.usgs.gov/ogw/aquiferbasics/).

Another set of studies has demonstrated that calcite may serve as a source for contaminants, which may be released during calcite dissolution (Kirsch et al., 2014). A batch experiment conducted by Lu et al. (2010) also suggested aquifers containing carbonate rocks were of particular concern due to the presence of Ba, Mn, and Sr in carbonates, in addition to increased alkalinity which followed carbonate dissolution. In addition, calcite was found to be the primary source for several released contaminants, such as As, Mn, and Ni, which exceeded regulatory limits in experiments conducted with limestone and dolomite aquifer materials (Wunsch et al., 2014; Wunsch et al., 2013). Other studies, although not in the context of CO_2 sequestration risk evaluation, have shown that while the calcite content can buffer the change in pH, As incorporated into the crystal lattice of carbonates such as calcite and those contained in limestone (Costagliola et al., 2013; Di Benedetto et al., 2006; Yokoyama et al., 2012), can be released as the carbonate minerals dissolve (Arthur et al., 2002; Lazareva et al., 2014).

Other minerals may serve as sources for contaminants when they undergo dissolution. Studies have focused on sandstone or unconsolidated sand and gravel aquifers (Fig. 5) with variable carbonate content (Cahill and Jakobsen, 2013; Carroll et al., 2009; Dafflon et al., 2013; Keating et al., 2010; Kharaka et al.,

2010; Kirsch et al., 2014; Spangler et al., 2010; Varadharajan et al., 2013; Yang et al., 2014; Zheng et al., 2012). The quantitative XRD analyses (QXRD) of the sediments from the High Plains aquifer showed that calcite contents of the sediments varied from ~0-4% , in addition to appreciable amounts of feldspars, montmorillonite, quartz, and mica (Lawter et al., 2015b). All these minerals may undergo dissolution under acidic conditions releasing their structural elements and potential contaminants into the aqueous phase. Other minerals (e.g., Fe oxides) may form when the aqueous phase becomes oversaturated as a result of dissolution; they may serve as sorbents for contaminant released during dissolution, although this topic has not received significant attention in the literature.

The solid phase chemistry of the aquifer rocks and sediments is important as well. The results from microwave digestions and 8M nitric acid extractions conducted with the High Plains aquifer sediments indicated that the solid phase of the sediments contained varied amounts of trace metals that are of environmental concern, such as As, Ba, Cd, Cr, and Pb, which are regulated with primary MCLs, and Fe, Mn, and Zn, which are regulated with secondary MCLs. Appreciable amounts of several contaminants (e.g., As) could be released from the sediments when contacted with CO_2 saturated groundwater (Lawter et al., 2015b; Qafoku et al., 2013). The same digestion analyses and extractions were conducted on the Edwards aquifer materials, and the results showed that they contained potentially releasable contaminants, including As, Cd, Cr, Pb, and Zn (Qafoku et al., 2013). Results of the batch and columns studies showed several of these contaminants, e.g., Cr, and Pb were released during the column experiments (Wang et al., 2016). These digestions and harsh extractions were conducted to determine the types of potential contaminants present in the sediments, which may (or may not) be mobilized when these solid materials are exposed to a CO_2 gas stream or CO_2 saturated brine.

2.4.2. Reservoir as a source of other relevant gases and inorganic and organic contaminants

In addition to CO_2, other gases (such as CH_4) or mixtures of gases may migrate together with the CO_2 and brine from storage reservoirs upwards to aquifers. While CH_4 can be present as an impurity in the injection CO_2 gas (Blanco et al., 2012; Mohd Amin et al., 2014), it can also be present as a native gas within the reservoir (Hosseini et al., 2012; Oldenburg and Doughty, 2011; Taggart, 2010), or could be produced in the reservoir through methanogenesis (Harvey et al., 2016; Leu et al., 2011). Experimental and modeling studies in this area are limited. An experimental study conducted with a 1% CH_4 and 99% CO_2 gas mix showed little effect of CH_4 on contaminant release (Lawter et al., 2015a). Other experiments were performed to investigate the effect of autotrophic methanogenesis stimulated by CO_2, on the mobility of metals (Harvey et al., 2016). Collectively, these tests were conducted to study the effect of gas, trace metal, and biological variations likely present in GCS sites on the release of contaminant under field relevant conditions. A modeling study by Mohd Amin et al. (2014) showed reduced transportation of acidic CO_2 saturated brine, resulting in reduced dissolution of the storage reservoir caprock when CH_4 was present. In another modeling study, Taggart (2010) created a model showing CO_2 driving out dissolved CH_4 from reservoir brine, creating a leading CH_4 plume that could be useful for monitoring leakage.

Reservoir brine, which may move upward with leaking CO_2, can also cause degradation of groundwater due to increased salinity. Chimayo, NM is the location of a natural analog site where shallow wells release CO_2 into an aquifer. Field studies coupled with modeling have been used to study the impact of CO_2 gas on the aquifer, as well as the transport of brine with CO_2 along fault zones (Keating et al., 2010; Keating et al., 2013a; Keating et al., 2013b). The Chimayo, NM site was compared with a site in Springerville, AZ, another natural analog site where brine is present but, in this case, the salinity of the affected aquifer was not significantly increased. Reactive transport models were used to determine what

conditions favor the transport of brine with CO_2, and found the width of the leakage pathway to be a major factor (i.e., narrow pathways increase co-transport) (Keating et al., 2013b).

Contaminants, such as As and Cd, originating from the reservoirs and from the rocks and/or sediments of different depths between the deep storage reservoirs and the aquifer, could travel upward with the leaking CO_2 and brine into the overlying aquifer. In a recent study, calcite-free sediments and sediments containing up to 4% calcite were used in batch and column experiments with an As and Cd spike (114 µg/L and 40 µg/L, respectively) added to the synthetic groundwater to determine contaminant fate if this were to happen (Lawter et al., 2015a; Lawter et al., 2015b). The concentration of As and Cd in the spike was based on maximum concentrations of these contaminants predicted to reach the aquifer from the brine source term within the reservoir, according to modeling simulations by Carroll et al. (2014a). Results showed the unconsolidated sand and gravel aquifer sediments had a large adsorption capacity for these contaminants, with a 90-95 % reduction of Cd and a 60-70% reduction of As within 4 hours in the gas injected reactors and a greater reduction in the blank (no gas) reactors (Lawter et al., 2015b).

Reservoir rocks are also a source of organic compounds within CO_2 storage sites. Field based demonstration sites have shown that CO_2 injection leads to greater dissolved organic carbon within sedimentary brine formations (Kharaka et al., 2006a) as well as increased concentrations of BTEX, PAHs, phenols and other toxic compounds in groundwater monitoring wells (Kharaka et al., 2009; Kharaka et al., 2010; Scherf et al., 2011; Spangler et al., 2010). Laboratory based experiments using both $scCO_2$ and organic solvents confirmed that reservoir rocks are sources of organic compounds and that the extractable organic material was dominated by n-aliphatic and aromatics (Jarboe et al., 2015; Kolak and Burruss, 2006; Kolak and Burruss, 2014; Kolak et al., 2015; Zhong et al., 2014a; Zhong et al., 2014b). In particular, n-alkanes ranging from n-C9 to n-C31 have been identified and have over 30 different aromatic compounds, including BTEX and naphthalene (Jarboe et al., 2015; Kolak and Burruss, 2014; Kolak et al., 2015; Zhong et al., 2014b). These laboratory based studies have also shown that the amount

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and type of extractable organic compounds was influenced by the solvent type (e.g., $scCO_2$ vs. dichloromethane), exposure duration, and the temperature and pressure of the extraction conditions as well as the source rock, water content, and geologic setting. Understanding the influence of the extraction parameters is crucial for understanding subsequent contaminant transport.

Mobilization of toxic organic compounds, including BTEX and PAHs, by $scCO_2$ has been reported in laboratory experiments for rock samples from depleted oil reservoirs, coal deposits (Zhong et al., 2014b), and sandstones (Scherf et al., 2011). Groundwater monitoring results from GCS demonstration sites have shown increased concentrations of BTEX, PAHs, phenols, and other toxic compounds in groundwater after CO_2 injection (Kharaka et al., 2009; Kharaka et al., 2010; Scherf et al., 2011; Spangler et al., 2010). Zhong et al. (2014a) focused on the transport and fate of toxic organic compounds mobilized by $scCO_2$ from organic rich storage reservoirs such as unmineable coal seams and depleted oil reservoirs. In these experiments, the coal sample contained a greater amount of extractable organics, with higher concentrations extracted with increased exposure duration. The $scCO_2$ extracted organics were then injected into column experiments containing a water wetted or dry sandstone core to study the potential for toxic organic compounds mobilized from coal by $scCO_2$ under simulated GCS conditions to impact groundwater. The results revealed that the mobility of the BTEX compounds through the core was much greater than for naphthalene (82% and 16% transported, respectively) under wet conditions. The retention of organic compounds from the vapor phase extract to the core appeared to be primarily controlled by partitioning from the vapor phase to the aqueous phase according to Henry's Law. Accordingly, reduced temperature and elevated pressure resulted in greater partitioning of the mobilized organic contaminants into pore water. Adsorption to the surfaces of the wetted sandstone was also significant for naphthalene. In another laboratory experiment, Kolak and Burruss (2014) found that under temperatures and pressures representing in situ coal bed storage conditions (40 ˚C and 100 bar), $scCO_2$ extracted the least amount of organic compounds from high volatile bituminous coals when compared to Soxhlet-dichloromethane and Soxhlet-carbon disulfide especially for organics with higher molecular weight and greater aromaticity.

Cantrell and Brown (2014) conducted a modeling study and found that when CO_2 was introduced into a reservoir with 90wt.% CO_2 and 10 wt.% oil, a significant fraction of the oil dissolved into the vapor phase. As the vapor phase moved up through the stratigraphic column, pressures and temperatures decreased, resulting in significant condensation of oil components. The heaviest organic components condensed early in this process (at higher pressures and temperatures), while the lighter components tended to remain in the vapor phase until much lower pressures and temperatures were reached. The final concentrations to reach an aquifer at 1,520 kPa and 25 $^\circ$C were quite significant for benzene and toluene, indicating that they could adversely impact groundwater quality (especially benzene) in the event CO_2 stored in a depleted oil reservoir leaks. Conversely, it was determined that CO_2 was unlikely to transport significant concentrations of PAHs to near surface depths, limiting their potential impact to groundwater. This is particularly true for the most carcinogenic of the PAH compounds, which are relatively heavy, making them prone to condensation from the vapor phase at much higher pressures and temperatures.

To include organic compounds in the reactive transport models, the compounds had to first be identified, and then the prospective concentrations of these compounds in the leaking CO_2 and brine had to be determined. Although the organic compounds present in deep saline aquifers have been seldom reported, the compositions in waters produced from oil fields have been extensively studied (RøeUtvik, 1999; Witter and Jones, 1999). BTEX, phenols, and PAHs have been identified as the organic compounds that were most likely to be leached out along with CO_2 as well as pose threats on the quality of shallow groundwater (Cantrell and Brown, 2014; Zheng et al., 2013). To simplify the model, benzene was used to represent BTEX, naphthalene to represent PAHs, and phenol to represent phenols. The respective maximum concentrations in the brine were taken from Zheng et al. (2010) , which were largely based on the concentration of these compounds in formation water from deep sedimentary basins (Kharaka and Hanor, 2007). The minimum concentrations were arbitrary. Around 500 simulations were conducted to account for the uncertainties of both flow and chemical parameters. The following graphs (Fig. 5) show pH and benzene results from one of the simulations to illustrate the spatial distribution of organic

compounds after 200 years of leakage. For details of other conditions of the model, refer to Carroll et al. (2014a). The key parameters used in this particular simulation are listed in Table 4.
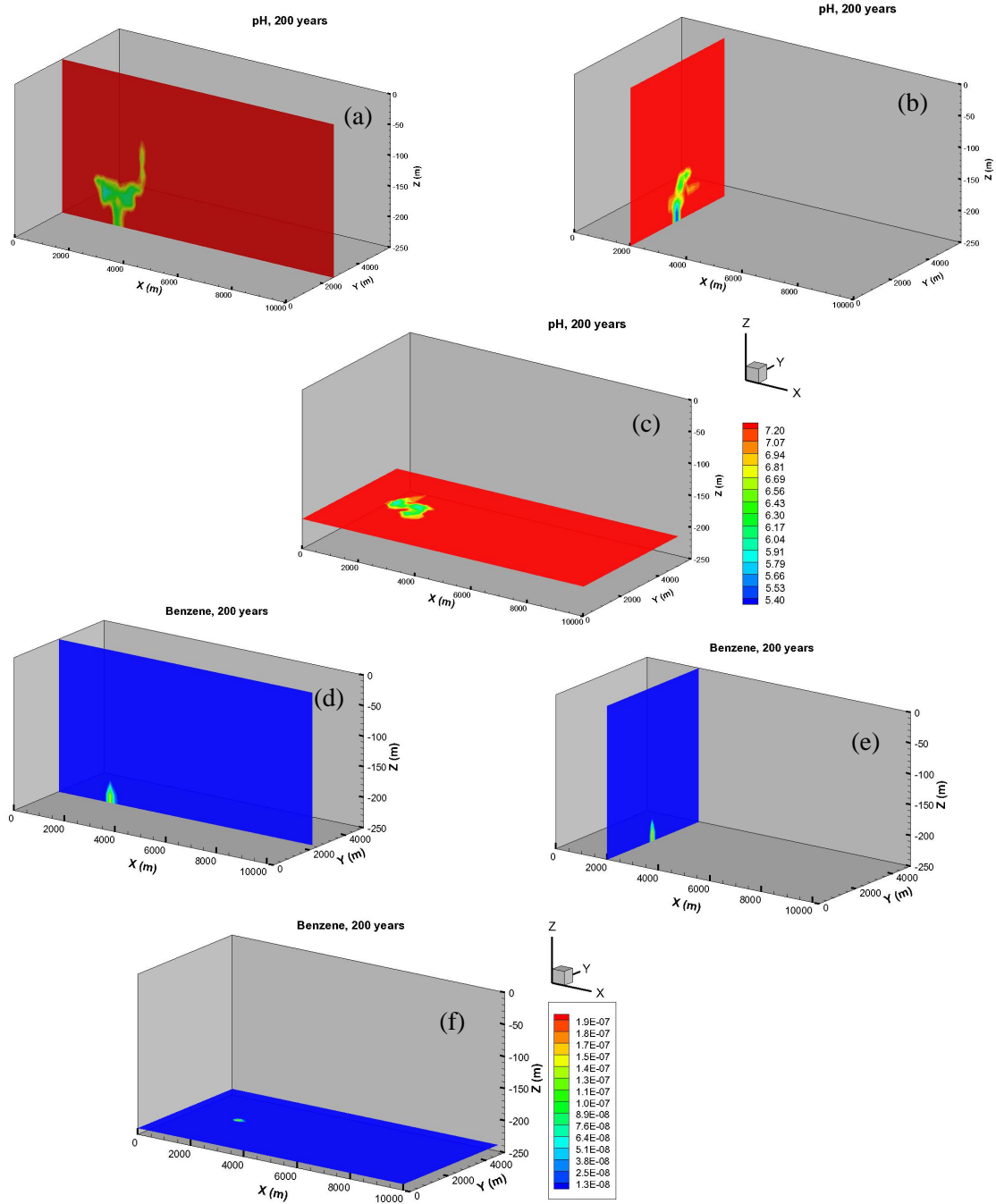

Figure 5. Cross Section Views of the Spatial Distribution of pH at 200 years. (a) at y=2600 m, (b) at x = 2000 m, and (c) at z = -202.5 m and Total Aqueous Benzene Concentration at 200 Years: (d) at y=2600 m, (e) at x = 2000 m, and (f) at z = -202.5 m (Lawter et al., 2015a).

Table 4. Flow and Chemical Parameters used in Simulations that Model Results

Parameter	Value
Benzene concentration in the leaking brine (mol/L)	2.51E-7
phenol concentration in the leaking brine (mol/L)	1.41E-7
Naphthalene concentration in the leaking brine (mol/L)	8.9E-8
Benzene distribution coefficient (L/kg)	1.24E-2
phenol distribution coefficient (L/kg)	1.18E-3
Naphthalene distribution coefficient (L/kg)	2.75E-1
Benzene degradation constant (1/s)	0
phenol degradation constant (1/s)	3.7E-7
Naphthalene degradation constant (1/s)	0

Simulation results showed the plumes of organic compounds were small compared to the plume of

pH, which is usually used to track the movement of CO_2. Despite the continuous leakage of brine that

contained a high concentration of benzene, the plume of benzene was fairly small and concentrated

around the leakage point. The naphthalene plume was even smaller because of adsorption and higher

distribution coefficient. Phenol had the smallest plume because of both adsorption and biodegradation. In

summary, modeling showed that the plumes of organic compounds were very small and could quickly

dissipate if the leakage stops, due to adsorption and biodegradation.

A similar modeling approach and the same compounds (i.e., benzene, naphthalene, and phenol) were

used by Bacon et al. (2014) to study the fate of these compounds leaking into the Edwards aquifer.

Adsorption was assumed to follow a linear adsorption isotherm, proportional to the organic carbon

content of the aquifer material, which was assumed to range between 0.1 and 1% by volume in the

limestone aquifer (Table 5).

Table 5. Input Parameters for Organic Adsorption and Biodegradation (Bacon et al., 2014)

Description	Minimum	Maximum	Units	Reference
Organic carbon volume fraction	1.00E-03	1.00E-02	—	Estimated
Benzene organic carbon partition coefficient	3.09E+01	5.37E+01	L/kg	(Lawrence, 2006)
Naphthalene organic carbon partition coefficient	9.93E+00	9.55E+02	L/kg	(Lawrence, 2006)

Phenol organic carbon partition coefficient	1.61E+01	3.02E+01	L/kg	(Boyd et al., 1983; Briggs, 1981)
Benzene aerobic biodegradation rate	1.00E-03	4.95E-01	day^{-1}	(Aronson et al., 1999)
Naphthalene aerobic biodegradation rate	6.40E-03	5.00E+00	day^{-1}	(Aronson et al., 1999)
Phenol aerobic biodegradation rate	6.00E-03	1.00E+01	day^{-1}	(Aronson et al., 1999)

The concentrations of benzene, naphthalene, and phenol in the leaking brine were assumed to be uncertain variables, with maximum concentrations ranging from 7.94E^{-5} to 6.31E^{-4} mol/L and minimum concentrations of 1.00E^{-10}. As part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program, the USGS collected and analyzed groundwater samples from 1996 to 2006 from the San Antonio segment of the Edwards aquifer (Musgrove et al., 2010). Initial concentrations of the organics in the aquifer were assumed to be zero, based on average aqueous concentrations for the 90 groundwater samples collected by the USGS (Musgrove et al., 2010). The volume of groundwater exceeding the threshold values for organic compounds was influenced significantly by biodegradation. Volumes of groundwater with concentrations greater than the benzene, naphthalene and phenol no-impact threshold values (see section 3.1) are relatively small (Fig. 6). By comparison, for the same set of simulations, the median pH-impacted aquifer volumes ranged from 1e^5 m^3 at 10 years to 1e^7 m^3 at 200 years.
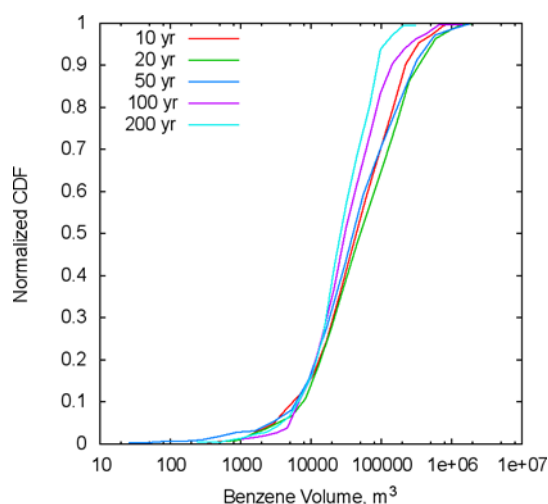

Figure 6. Cumulative density function of aquifer volume exceeding benzene no-impact thresholds during 200 years of well leakage (Lawter et al., 2015a).

3.0   Conceptual and Reduced Order Models to Assess and Predict Aquifer Responses to CO₂ and Brine Leakage

Development of adequate conceptual models and measurement of key parameters are both critical activities when it comes to determining risks to aquifer quality due to CO_2 and brine leakage. Conceptual models and groundwater ROMs include the following set of data: 1.) Initial groundwater elemental concentrations and threshold values; 2.) Site mineralogy and chemistry (e.g., calcite, Si bearing minerals, contaminants sorbed or part of mineral crystal structure, etc.); and 3.) Relevant hydrological and geochemical processes and reactions related to the impact of CO_2 gas and brine on groundwater quality, and those that control the fate of chemical elements released from rocks and sediments and/or transported with the brine from deep reservoirs (e.g., dissolution/precipitation, incorporation in mineral structures, adsorption/desorption and electron transfer, etc.). Thermodynamic data (log K's) for rock mineral and aqueous complexes, surface complexation reactions for trace metals, and K_{oc} and biodegradation rates for organic compounds and other key parameters are also required for the modeling efforts. In addition, the degree of impact (i.e., significant or insignificant changes in pH and major, minor, and trace element releases) would depend on other controlling variables such as leaking plume characteristics [e.g., gas composition (pure CO_2 and/or CO_2 -CH_4 -H_2S mixtures) and brine concentration and composition]. Two recent studies have looked at making ROMs faster and less costly (Keating et al., 2016c) and provided guidance on how and when to use previously developed ROMs (Keating et al., 2016b).

3.1   Threshold values and average groundwater concentrations

In order to determine whether CO_2 and brine leakage has an impact on groundwater quality, a protocol needs to be established for determining statistically significant changes in groundwater concentrations of regulated contaminants (Last et al., 2013). The study by Last et al. (2013) examined selected portions of the urban shallow-unconfined aquifer system of the Edwards aquifer and a portion of

the High Plains aquifer. No-impact threshold values were determined for Cd, Pb, As, Cr, pH, TDS, and select organic compounds that could be used to identify potential areas of contamination predicted by numerical models of storage reservoirs. These threshold values were based on an interwell approach for determining background groundwater concentrations as recommended in the U.S. Environmental Protection Agency's document titled: "Unified Guidance for Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities (2009)". The no-impact threshold values can be used to inform a "no change" scenario with respect to groundwater impacts, rather than using a MCL or secondary drinking-water standard that in some cases could be significantly higher than existing concentrations in the aquifer.

Development of "generic" no-impact threshold values that could be used for a number of locations appears unlikely. Instead, the threshold values must be based on site-specific groundwater quality data. However, the scarcity of existing data, proximity of the data to the target model domain, potential spatial heterogeneity, and temporal trends make the development of statistically robust data sets and the use of valid statistical assumptions challenging. In some cases, the calculated no-impact threshold values may exceed regulatory standards. Other approaches, such as the hybrid intrawell-interwell approach also examined in the study by Last et al. (2013) may provide alternate mechanisms for calculating no-impact threshold limits. Examples are presented in the following sections to demonstrate the development and use of threshold values in two representative aquifers, the High Plains and Edwards aquifers.

The hydrology ROMs and chemical scaling functions generated in the Generation III ROM (Zheng et al., 2014) were specific to threshold values that represent no net degradation to the groundwater quality. The impact thresholds defined for pH, TDS, trace metals, and select organics in Table 6 represent concentrations above (or below for pH) the background water chemistry that could be used to assess impact from brine and/or CO_2 leakage into the aquifer. Each threshold was calculated as the 95%-confidence, 95%-coverage tolerance from data collected in a 2010 USGS groundwater survey of 30 wells within the High Plains aquifer from an area outside of the lithology model site.

Table 6. Initial aquifer concentrations used in the simulations, estimated mean aquifer values, and no-impact thresholds (Carroll et al., 2014a)

Parameter	Initial Value Used in Third-Generation Simulations	Mean of Selected and Adjusted 2010 Data[b]	"No-Impact" Threshold[c]	U.S. EPA Regulatory Standard
pH	7.6[a]	7.5[c]	7.0	6.5
TDS	570 mg/L[a,d]	440 mg/L[d]	1,300 mg/L[d,e]	500 mg/L[e]
Arsenic	1.50 µg/L	1.50 µg/L	9.30 µg/L	10.00 µg/L
Barium	43.00 µg/L[b]	43.00 µg/L[b]	140.00 µg/L	2,000 µg/L
Cadmium	0.06 µg/L	0.06 µg/L	0.25 µg/L	5 µg/L
Chromium	1.00 µg/L	1.00 µg/L	3.90 µg/L	100 µg/L
Iron	5.40 µg/L[b]	5.40 µg/L[b]	43.00 µg/L[b]	300 µg/L
Lead	0.09 µg/L	0.09 µg/L	0.63 µg/L	15 µg/L
Manganese	0.35 µg/L[d]	0.35 µg/L[d]	7.00 µg/L[d]	50 µg/L
Benzene	0	<0.03 µg/L[d]	0.03 µg/L[g]	5 µg/L
Naphthalene	0	<0.20 µg/L[d]	0.20 µg/L[g]	700 µg/L
Phenol	0	<0.003 µg/L[f]	0.003 µg/L[g]	10,000 µg/L[h]

(a) Based on Carroll et al., 2009.
(b) Geometric mean except for pH.
(c) 95%-confidence, 95%-coverage tolerance limit based on log values except for pH.
(d) Rounded to two significant digits.
(e) Threshold value exceeds regulatory standard; using the regulatory standard may result in widespread false positives under field conditions.
(f) As 4-Chloro-2-methylphenol.
(g) Detection limit for the 2010 U.S. Geologic Survey National Water-Quality Assessment Program (NAWQA) sample data.
(h) Recommended Water Quality Criteria for Human Health, consumption of Water + Organism (74 FR 27535);
http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#hhtable.

This data set was chosen because spatial and temporal data were not available from wells located within the model domain. Benzene, naphthalene, and phenol were used as representatives of BTEX, pPAHs, and phenol organic compounds that could be present in the leaking brine (Zheng et al., 2010). Regulatory standards referring to concentrations that exceed primary or secondary maximum contaminant levels designated by the EPA (2009) were also used when available.

The "no-impact" threshold values were also developed for the Edwards aquifer. Ninety water samples from the shallow, unconfined portion of the Edwards aquifer in Texas, collected as part of the NAWQA Program (Musgrove et al., 2010), were used to examine methodologies for establishing baseline data sets and protocols for determining statistically significant changes between background concentrations and predicted concentrations that would be used to represent a contamination plume in

modeling simulations (Last et al., 2013). Initial values of As, Ba, Cd, Pb, benzene, naphthalene, phenol, pH, and TDS concentrations were also determined using selected statistical methods (Table 7; the EPA MCLs are also shown for comparison). The no-impact thresholds, determined for a specific aquifer, are useful as they allow for better prediction of potential impacts to an aquifer, as opposed to using regulatory standards, such as MCLs.

Table 7. Initial values, tolerance limits, and regulatory standards for each variable (Last et al., 2013; Lawter et al., 2015a)

Analyte	Initial Value	"No-Impact" Threshold	Maximum Contaminant Level	Units
Arsenic	0.31	0.55	10	µg/L
Barium	38	54	2000	µg/L
Cadmium	0	0.04	5	µg/L
Lead	0.064	0.15	15	µg/L
Benzene	0	0.016	5	µg/L
Naphthalene	0	0.4	0.20	µg/L
Phenol	0	0.005	10000	µg/L
pH	6.9	6.6	6.5	$-\log[H^+]$
TDS	330	420	500	mg/L

3.2   Relevant processes and reactions

The most important reactions that may affect pH, TDS, trace metals, and organic compounds in the aquifers are included in three groups and discussed in this section; however, it is likely that only a subset of these reactions will be important for a particular aquifer.

3.2.1   Adsorption and desorption

This group of reactions includes adsorption/ion exchange and desorption reactions (Apps et al., 2010; Kharaka et al., 2006a; Kharaka et al., 2009; Zheng et al., 2009). In typical aquifer materials, Fe oxides and hydroxides, Al oxides and phyllosilicates are important adsorbents, although other minerals could also serve as adsorbents. For example, Zheng et al. (2012) summarized the surface protonation reactions and adsorption and desorption reactions of Cd, Cu, Pb, As, Ca, Fe, Ba, Cr, Sb, and aqueous carbonate on

goethite, illite, kaolinite, and montmorillonite. These reactions can be modeled with a linear adsorption isotherm model (using the distribution coefficient, K_d, as the key parameter) or a surface complexation model (SCM), which was used to model the adsorption and desorption of trace metals in the Edwards and High Plains aquifer materials (Bacon et al., 2016; Zheng et al., 2016). Linear adsorption isotherm studies which are widely used in geochemical studies of different types are also used in CO_2 related studies. The large range of measured K_d values in studies conducted with organic compounds is primarily due to the dependence of K_d on the organic matter content in the initial material, which can be quite variable. In other words, K_d is a site specific parameter, and the same K_d value is not necessarily appropriate for a range of different aquifers. However, although the K_d depends on the properties of sediments, the hydrophobic partitioning theory as reviewed by Karickhoff et al. (1979) indicates that the partitioning of a specific compound between water and organic carbon, i.e., K_{oc}, is largely independent of the organic content of the solid material.

3.2.2 Dissolution and precipitation

This group of chemical reactions is critical for determining how an aquifer responds to incoming CO_2 and brine concentrations, and include, among others, the dissolution of carbonates (Birkholzer et al., 2008; Kharaka et al., 2006b; McGrath et al., 2007), sulfides (Apps et al., 2010; Wang and Jaffe, 2004; Zheng et al., 2009), and Fe oxyhydroxide minerals (Kharaka et al., 2006a; Kharaka et al., 2009). The dissolution of minerals is the major pH buffering process, as is demonstrated in this paper. In addition, the dissolution of minerals could lead to the release of trace metals directly or indirectly. For example, the dissolution of some sulfide minerals (e.g., galena or arsenopyrite) resulted in an increase of aqueous Pb and As concentrations (Apps et al., 2010; Wang and Jaffe, 2004; Zheng et al., 2009) and the dissolution of calcite resulted in the release of Sr and Ba (Lu et al., 2010). The dissolution of calcite could also cause indirect release of Cs and Ba by triggering Ca-driven cation exchange reactions (Zheng et al., 2012). It is noteworthy that not only the fast reacting minerals such as calcite play a significant role, but also the slow reacting minerals, in certain circumstances, may contribute to the release of contaminants. For instance,

Trautz et al. (2013) showed in a field test in Mississippi that the dissolution of plagioclase (which usually dissolves at a much slower rate than calcite) started to release calcium and subsequently triggered the increase in concentrations of Sr and Ba via cation exchange reactions, after the injection of CO_2-saturated water stopped. One should emphasize that the fast and slow dissolution reactions are part of the complex chemical reaction networks established in the aquifers when it is exposed to the CO_2 gas and brine. It is therefore necessary to take into account all of the minerals phases when developing a reactive transport model, despite the fact that most of the time a subset of these minerals is selected due to pragmatic reasons, such as computation time. Examples of minerals and their kinetic reaction rates used in models can be found in Zheng et al. (2016) and Bacon et al. (2016) for the High Plains and Edwards aquifers, respectively.

3.2.3 Redox reactions

Redox potential is a very important parameter that controls the fate of redox-sensitive trace metals and organic compounds when groundwater of an aquifer is affected by the leakage of CO_2 (Harvey et al., 2013). For example, it is known that As(III) has much higher mobility and is more environmentally concerning than As(V). Also, the biodegradation rate for an organic compound is much higher in oxidizing than reducing conditions. When CO_2 or CO_2-saturated brine leaks into the aquifer, pH decreases almost immediately but Eh changes as well due to the interrelation of pH and Eh. It is therefore critical to know the initial Eh in the aquifer and the change after the intrusion of CO_2. For confined aquifers, because of the fairly low redox potential, a sufficient increase in redox potential to cause a shift of speciation of redox-sensitive species, such as As, is unlikely. For unconfined aquifers, changes in redox potential are more likely and could shift the speciation and key parameters of potential contaminants (e.g., degradation rate for organic compounds). However, in either case, redox reactions have to be included in the reactive transport models and redox potentials have to be determined.

3.3 Development of conceptual and reduced order models

The development of a ROM requires multiple runs of the reactive transport models that simulate the leakage of CO_2 and brine into a shallow aquifer. The core of the reactive transport model is the geochemical conceptual model. In order to develop a defensible conceptual model, *__first,__* detailed groundwater chemical and mineral composition data are needed, and the cation exchange capacity (CEC) and sorption capacity of the aquifer sediments need to be measured. Based on this input, the geochemical equilibrium calculations will then reveal the mineral phases and reactions that control major and trace elemental aqueous concentrations, pH and Eh. *__Second,__* well-mixed batch experiments should be conducted to determine elemental release maxima and trends (i.e., if an element is not released in batch experiments, it is unlikely to be released in large scale aquifers) (Zheng et al., 2015). The results of batch experiments combined with geochemical modeling are also used to select the set of chemical reactions that control the release of trace elements. One should emphasize, however, that because of the nature of the batch experiments, some reactions that may be relevant under those conditions may become less important, or even irrelevant, under aquifer conditions. *__Third__*, it is desirable to conduct column experiments to evaluate transport parameters, such as those conducted with High Plains (Lawter et al., 2015b; Lawter et al., 2016) or Edwards (Wang et al., 2016) aquifer sediments. Because of the larger solid to solution ratio, such tests provide more realistic estimates of the release of elements and their concentrations as a result of the introduction of CO_2 into an aquifer. A reactive transport model for the column test (Zheng et al., 2016) can further narrow down the key reactions and parameters and lay a strong foundation for a reactive transport model at appropriate field scales.

After the establishment of the conceptual model, simulations can be conducted for the time steps and spatial resolution needed. A sensitivity analysis is conducted first to determine which parameters contribute most to model uncertainty. The development of the Gen III hydrology ROM (Carroll et al., 2014a) is an example of the procedure to develop a ROM. *__First__*, the parameter ranges need to be determined for the development of the aquifer model, hydrologic flow, leakage flux, brine concentrations,

and geochemical parameters. ***Second***, these parameters are selected and used to design a number of simulations. For example, for the Gen III hydrology ROM (Carroll et al., 2014a), 1000 simulations were conducted, using random samples of each of the input parameters within specified ranges. ***Third,*** model results are processed to calculate the entities used to build the ROM and then the ROM is derived. Depending on the nature of the ROM (e.g., polynomial-based ROMs, lookup tables, etc.), the derivation method is different. The ROM should be able to emulate the outcome of the numerical model, but with less complexity, more thorough sampling of the parameter space, and significantly faster simulation times to generate risk-based profiles that can be used in decision making processes. To develop groundwater ROMs, the threshold values, initial groundwater concentrations, rock mineralogy, thermodynamic data for rock mineral and aqueous complexes, surface complexation reactions for trace metals, and K_{oc} and biodegradation rates for organics are all required. Parameters needed to drive the Gen II and III ROMs can be grouped in three categories: parameters that are related to the source term, parameters to define the hydrological properties of the aquifer, and parameters used to define the chemical properties of the aquifer.

4.0   Conclusive Remarks

Leakage of CO_2 from storage reservoirs is a primary risk factor and a potential barrier to the widespread acceptance of geologic CO_2 sequestration. A systematic understanding of how CO_2 and/or brine leakage would affect the quality of potable aquifers, and subsequently control or affect contaminant release via dissolution, desorption, and/or redox reactions, is vital. A summary of the crucial site-specific data needed to determine whether the leaked CO_2 will affect the groundwater quality and future research needs are included below.

4.1 Crucial site-specific data and models

Essential site-specific data needed to estimate the potential impacts of CO_2 and brine plumes on aquifer quality are:

1. *The no-impact threshold values* can be used to inform a "no change" scenario with respect to groundwater impacts. In some cases, the calculated no-impact threshold values may exceed regulatory standards. For homogeneous aquifers with low concentrations of dissolved solids (i.e., those with little variability and low background values) there will be a higher likelihood that the threshold values will be exceeded should leakage occur. For instance, in the Edwards aquifer, it would only take a leak of 10 MT of CO_2 into the aquifer to push the concentration of lead above the no-impact threshold value of 0.15 μg/L [NRAP AIM v2016.04-1.1.4 (Keating et al., 2016a)].

2. *The salinity, trace metal, and organic content of reservoir fluids.* The contaminants of concern will depend on the characteristics of the reservoir brine, and whether there are significant differences between the reservoir pore water composition and the drinking water aquifer. For example, it would take a leak of 5 MT of reservoir brine into the Edwards aquifer to increase the As concentration above the no-impact threshold value of 0.55 μg/L or to exceed the no-impact threshold of 9.30 μg/L in the High Plains aquifer [NRAP AIM v2016.04.1.1.4 (Keating et al., 2016a)]. It is important to determine the amount of organic matter and aquifer biodegradation potential to predict the persistence of the organic contaminants coming from the reservoirs. Establishing the redox potential of the aquifer is also important because biodegradation rates tend to be higher in oxidizing environments. Based on biodegradation rates and sorption coefficients from the literature, organic plumes are not expected to persist in groundwater; experiments are needed to confirm this under site-specific conditions.

3. *The calcite (and other mineral) content.* There is a significant difference in the impact to pH on the High Plains aquifer samples with and without calcite present (~1 pH unit). As expected, the

Edwards aquifer limestone, which consists mainly of calcite, shows a strong capacity to buffer pH changes due to interaction with CO_2. Other minerals could dissolve under low pH conditions and contribute to increased TDS and/or trace metal concentrations. The dissolution of galena, for example, could cause increases in Pb concentrations above background levels.

4. *The amount and type of sorbents.* In the Edwards aquifer, adsorption to calcite controls the release of trace metals upon exposure to CO_2 and a subsequent decrease in aqueous pH. In a sand and gravel aquifer like the High Plains, Fe oxides and hydroxides and phyllosilicates are important adsorbents.

5. *The mass of CO_2 or brine leaked* is directly proportional to the risk to groundwater (i.e., changes in pH, TDS, trace metals and organic compound concentrations). In many simulations the leaked mass is relatively small and plumes are not likely to be detected by the pumping of existing groundwater wells [see for example: Keating et al. (2014a)]. However, even with small leaks, zones of lowered pH and elevated TDS and trace metals may persist for decades.

6. *Site-specific ROMs* can be developed to describe and predict aquifer response to CO_2 and brine leakage. Due to their low computation requirements, these models can be used to quickly estimate the degree of impact in terms of changes in pH, and major, minor, and trace element releases based on a range of aquifer properties (e.g., initial aqueous concentration, mineralogy, etc.), changes in solid phase chemistry and mineralogy, leaking plume characteristics (gas composition, such as pure CO_2 and/or CO_2-CH_4 -H_2S mixtures), and brine concentration and composition. The ROMs are also able to predict the degree of impact, whether the changes in the aquifer are significant or insignificant, the fate of the elements released from sediments or transported with brine, and are based on the extent and rate of reactions such as precipitation/incorporation into minerals (calcite and other minerals), adsorption, electron transfer reactions, and the role of natural attenuation. Some applications of these models and various field studies indicate that

there are cases where there could be measurable, long-term impacts to groundwater due to CO_2 or brine leaks.

7. *Field-scale models* of CO_2 and brine leakage, driven by models of CO_2 injection into a reservoir and leakage via abandoned wellbores of varying permeability, for the High Plains aquifer and shallow, urban unconfined portion of the Edwards aquifer, were used to calculate the volume of the aquifer above background threshold values for various parameters due to CO_2 leaks of different rates. The volume of the impacted aquifer is very sensitive to the threshold value used; in most cases the regulatory threshold (EPA MCL) is significantly less limiting than the threshold value indicated by the background variability in aquifer concentrations, and so groundwater impacts are more pronounced when utilizing these no-impact thresholds. When comparing the volumes of each of the two aquifers impacted by elevated trace metal concentrations, we find that although initial adsorbed trace metal concentrations are lower in the Edwards sediments than the High Plains sediments, the background variability of the shallow, urban unconfined portion of the Edwards aquifer is low compared to the High Plains aquifer, leaving it more vulnerable to changes in groundwater quality due to CO_2 or brine leakage. A parameter sensitivity analysis shows that groundwater impacts are more sensitive to the leak rates of CO_2 and brine and hydraulic aquifer characteristics, such as permeability and groundwater flow rate, than to geochemical parameters, such as mineral dissolution rate, with the exception of the presence of calcite in the aquifer sediments.

4.2   Future efforts

Although a number of laboratory and field experiments, as well as, modeling studies have been conducted to investigate the impact of CO_2 and brine leakage on groundwater quality, which has greatly enhanced our understanding of the magnitude of such impacts and their controlling processes, several key questions still remain, and further investigations are required.

1. ***A remaining question is whether trace metal releases due to leaking CO_2 are harmful***. It could be argued that a small increase in the concentration of a trace metal, such as Pb, above the no-impact threshold value in an aquifer will not have a measureable health impact. However, assessing potential health impacts was not a focus of this study. The EPA has established MCL thresholds to protect human health. Long-term increases above the MCL thresholds could therefore have the potential for negative impacts on human health. The scientific community has not yet reached an agreement on the important issue of deciding whether the impacts are negative, insignificant, or positive. One reason could be that the degree of perturbation and response to induced changes is site-specific and a function of inherent aquifer properties as well as the characteristics of the leaking plume (i.e., gas composition and brine concentration) at the specific site.

2. Two of the remaining questions to be addressed as investigations move to the post-injection site care period are: ***once leakage is detected and stopped, will concentrations of trace metals released recover to the background (pre-leakage) level of the aquifer; and at what times scales will this happen in comparison with the recovery of pH and dissolved CO_2***? Once the leakage stops, the CO_2 plume (dissolved or gaseous) and corresponding region of decreased pH will be diluted due to mixing with groundwater. As a result, the gaseous CO_2 will dissolve, and eventually, dissolved CO_2 will be present at a very low concentration. While it may not reach pre-leakage conditions, the concentration may become low enough to allow the aqueous pH of the aquifer to return to ambient conditions. Nevertheless, modeling studies (Zheng et al., 2015) and laboratory experiments (Fox et al., 2014) show that trace metals have fairly complex behavior in terms of recovery. Further studies are certainly warranted. Numerical simulations supported with laboratory experiments should be conducted to address this issue.

3. Organic contaminants mobilized from the injection reservoir were considered in development of the groundwater impact models for the High Plains and Edwards aquifers. ***However, it is not***

known how these contaminants may partition between the CO_2 saturated aqueous and air phases as they travel up a borehole or other leakage pathways. Experiments are needed to determine how changes in pressure and temperature along the leakage path(s) will affect phase partitioning of these contaminants, as the modeling work by Cantrell and Brown (2014) began to do. This will impact their long-term persistence once they arrive in the aquifer. Studies are also needed to determine the extent and rate of major and minor element release in the leakage pathway(s) (i.e., from deep reservoirs to aquifers) under conditions of decreasing temperature and pressure.

4. While ROMs have been demonstrated as an effective tool to evaluate the risk associated with groundwater, *the development of such models is challenging mainly because of the highly non-linear response of the impacted volume to changes in chemical parameters*. For example, there is a chance, albeit less common, that the aquifer sediments are very low in calcite content and calcite is removed due to dissolution, which would cause the volume of pH greater than the threshold to change sharply; this process is difficult for ROMs to emulate. One potential solution is to further categorize aquifer conditions and develop ROMs for each condition. In addition to ROMs currently developed for the Edward and High Plains aquifers, which are both aquifers with appreciable pH buffering capacity, a ROM for aquifers with limited pH buffering capacity is desirable. An integrated experimental and numerical investigation of CO_2 reactive transport in different types of shallow aquifers is needed to further explore the CO_2-realted geochemical reaction mechanisms and accurately quantify the uncertainty of the risk/impact factors.

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5.0   References

Altevogt, A.S., Jaffe, P.R., 2005. Modeling the effects of gas phase CO2 intrusion on the biogeochemistry of variably saturated soils. Water Resources Research, 41.

Annunziatellis, A. et al., 2008. Gas migration along fault systems and through the vadose zone in the Latera 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 CO_2 leakage from deep geologic storage. Transport Porous Med., 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.

Aronson, D., Citra, M., Shuler, K., Printup, H., Howard, P.H., 1999. Aerobic Biodegradation of Organic Chemicals in Environmental Media: A Summary of Field and Laboratory Studies, U.S. EPA, North Syracuse, New York.

Arthur, J., Dabous, A., Cowart, J., 2002. Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. In: Aiken, G.R., Kuniansky, E.L. (Editors), U.S. Geological Survey artificial recharge workshop. USGS, Sacramento, California.

Bachu, S., 2008. CO_2 Storage in Geological Media: Role, Means, Status, and Barriers to Deployment. Progress in Energy and Combustion Science, 34: 254-273.

Bacon, D., Qafoku, N., Dai, Z., Keating, E., Brown, C., 2016. Modeling the Impact of Carbon Dioxide Leakage into an Unconfined, Oxidizing Carbonate Aquifer. International Journal of Greenhouse Gas Control, 44: 290-299.

Bacon, D.H., Dai, Z., Zheng, L., 2014. Geochemical Impacts of Carbon Dioxide, Brine, Trace Metal and Organic Leakage into an Unconfined, Oxidizing Limestone Aquifer. Energy Procedia, 63: 4684-4707.

Birkholzer, J.T. et al., 2008. Research project on CO_2 geological storage and groundwater resources, quality effects caused by CO_2 Intrusion into Shallow Groundwater, Technical Report, Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

Blanco, S.T., Rivas, C., Fernandez, J., Artal, M., Velasco, I., 2012. Influence of Methane in CO2 Transport and Storage for CCS Technology. Environmental Science & Technology, 46(23): 13016-13023.

Boyd, S.A., Shelton, D.R., Berry, D., Tiedje, J.M., 1983. Anaerobic Biodegradation of Phenolic-Compounds in Digested-Sludge. Appl Environ Microb, 46: 50-54.

Briggs, G.C., 1981. Theoretical and Experimental Relationships between Soil Adsorption, Octanol-Water Partition- Coefficients, Water Solubilities, Bioconcentration Factors, and the Parachor. J. Agric. Food Chem., 29: 1050-1059.

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.

Cantrell, K.J., Brown, C.F., 2014. Source term modeling for evaluating the potential impacts to groundwater of fluids escaping from a depleted oil reservoir used for carbon sequestration. International Journal of Greenhouse Gas Control, 27: 139-145.

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.

Carroll, S.A. et al., 2014a. Reduced-Order Model for Estimating Impacts from CO2 Storage Leakage to Alluvium Aquifers: Third-Generation Combines Physical and Chemical Processes, NRAP Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2014; p XX.

Carroll, S.A. et al., 2014b. Key factors for determining groundwater impacts due to leakage from geologic carbon sequestration reservoirs. International Journal of Greenhouse Gas Control, 29(0): 153-168.

Celia, M.A., Nordbotten, J.M., 2009. Practical modeling approaches for geological storage of carbon dioxide. Ground Water, 47(5): 627-638.

Costagliola, P. et al., 2013. Arsenic-Bearing Calcite in Natural Travertines: Evidence from Sequential Extraction, mu XAS, and mu XRF. Environmental Science & Technology, 47(12): 6231-6238.

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. 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.

Di Benedetto, F. et al., 2006. Arsenic incorporation in natural calcite lattice: Evidence from electron spin echo spectroscopy. Earth and Planetary Science Letters, 246(3–4): 458-465.

DOE, 2007. Carbon Sequestration Technology Roadmap and Program Plan, U.S. DOE and NETL, Washington DC.

Fox, P.M., Nico, P.S., Davis, J.A., Spycher, N., 2014. Impact of elevated CO2 on release of trace elements from aquifer sediments of the San Joaquin Valley, CA, AGU fall meeting.

Frye, E., Bao, C., Li, L., Blumsack, S., 2012. Environmental Controls of Cadmium Desorption during CO2 Leakage. Environmental Science & Technology, 46(8): 4388-4395.

Harvey, O.R. et al., 2013. Geochemical Implications of Gas Leakage associated with Geologic CO2 Storage-A Qualitative Review. Environ. Sci. Technol., 47(1): 23-26.

Harvey, O.R., Qafoku, N.P., Cantrell, K.J., Wilkins, M.J., Brown, C.F., 2016. Methanogenesis-induced pH–Eh shifts drives aqueous metal(loid) mobility in sulfide mineral systems under CO2 enriched conditions. Geochimica et Cosmochimica Acta, 173: 232-245.

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.

Horner, K.N., Schacht, U., Haese, R.R., 2015. Characterizing long-term CO2-water-rock reaction pathways to identify tracers of CO2 migration during geological storage in a low-salinity, siliciclastic reservoir system. Chemical Geology, 399: 123-133.

Hosseini, S.A., Mathias, S.A., Javadpour, F., 2012. Analytical Model for CO2 Injection into Brine Aquifers-Containing Residual CH4. Transport in Porous Media, 94(3): 795-815.

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.

Jacquemet, N. et al., 2011. Intrusion of CO2 and impurities in a freshwater aquifer-impact evaluation by reactive transport modelling. 10th International Conference on Greenhouse Gas Control Technologies, 4: 3202-3209.

Jarboe, P.J., Candela, P.A., Zhu, W.L., Kaufman, A.J., 2015. Extraction of Hydrocarbons from High-Maturity Marcellus Shale Using Supercritical Carbon Dioxide. Energy & Fuels, 29(12): 7897-7909.

Jones, D. et al., 2015. Developments since 2005 in understanding potential environmental impacts of CO 2 leakage from geological storage. International Journal of Greenhouse Gas Control, 40: 350-377.

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.

Jun, Y.-S., Giammar, D.E., Werth, C.J., 2013. Impacts of geochemical reactions on geologic carbon sequestration. Environ. Sci. Technol., 47(1): 3-8.

Karickhoff, S.W., Brown, D.S., Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. Water Research, 13(3): 241-248.

Keating, E., Bacon, D., Carroll, S., Mansoor, K., 2016a. Aquifer Impact Model (AIM) Tool User's Manual, Version: 2016.04-1.1.4, National Energy Technology Laboratory, Morgantown, WV.

Keating, E. et al., 2016b. Applicability of aquifer impact models to support decisions at CO2 sequestration sites. International Journal of Greenhouse Gas Control, 52: 319-330.

Keating, E., Dai, Z., Dempsey, D., Pawar, R., 2014a. Effective detection of CO2 leakage: a comparison of groundwater sampling and pressure monitoring. Energy Procedia, 63: 4163-4171.

Keating, E., Newell, D., Dempsey, D., Pawar, R., 2014b. Insights into interconnections between the shallow and deep systems from a natural CO2 reservoir near Springerville, Arizona. International Journal of Greenhouse Gas Control, 25: 162-172.

Keating, E.H., 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 Sciences, 60(3): 521-536.

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., Harp, D.H., Dai, Z., Pawar, R.J., 2016c. Reduced order models for assessing CO 2 impacts in shallow unconfined aquifers. International Journal of Greenhouse Gas Control, 46: 187-196.

Keating, E.H. et al., 2013b. CO2/Brine Transport into Shallow Aquifers along Fault Zones. Environmental Science & Technology, 47(1): 290-297.

Kharaka, Y.K. et al., 2006a. Gas-water-rock interactions in Frio Formation following CO2 injection: Implications for the storage of greenhouse gases in sedimentary basins. Geology, 34(7): 577-580.

Kharaka, Y.K., Cole, D.R., Thordsen, J.J., Kakouros, E., Nance, H.S., 2006b. Gas-water-rock interactions in sedimentary basins: CO2 sequestration in the Frio Formation, Texas, USA. Journal of Geochemical Exploration, 89(1-3): 183-186.

Kharaka, Y.K., Hanor, J.S., 2007. Deep fluids in the continents: I. sedimentary basins. In: Drever, J.I. (Ed.), Surface and Ground Water, Weathering and Soils. Elsevier, Treatise on Geochemistry, pp. 1-48.

Kharaka, Y.K. et al., 2009. Potential environmental issues of CO2 storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA. Applied Geochemistry, 24(6): 1106-1112.

Kharaka, Y.K. et al., 2010. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO_2 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.

Kolak, J.J., Burruss, R.C., 2006. Geochemical investigation of the potential for mobilizing non-methane hydrocarbons during carbon dioxide storage in deep coal beds. Energy & Fuels, 20(2): 566-574.

Kolak, J.J., Burruss, R.C., 2014. The use of solvent extractions and solubility theory to discern hydrocarbon associations in coal, with application to the coal-supercritical CO2 system. Organic Geochemistry, 73: 56-69.

Kolak, J.J., Hackley, P.C., Ruppert, L.F., Warwick, P.D., Burruss, R.C., 2015. Using Ground and Intact Coal Samples To Evaluate Hydrocarbon Fate during Supercritical CO2 Injection into Coal Beds: Effects of Particle Size and Coal Moisture. Energy & Fuels, 29(8): 5187-5203.

Last, G.V. et al., 2013. Determining threshold values for identification of contamination predicted by reduced order models, Pacific Northwest National Laboratory, Richland, WA.

Lawrence, S.J., 2006. Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water — A Review of Selected Literature, U.S. Geological Survey, Reston, Virginia.

Lawter, A., Qafoku, N., Shao, H., Bacon, D., Brown, C., 2015a. Evaluating Impacts of CO2 and CH4 Gas Intrusion into an Unconsolidated Aquifer: Fate of As and Cd. Frontiers in Environmental Science, 3(49).

Lawter, A., Qafoku, N.P., Shao, H., Bacon, D., Brown, C., 2015b. Evaluating Impacts of CO2 and CH4 Gas Intrusion into an Unconsolidated Aquifer: Fate of As and Cd. Frontiers in Environmental Science, 3.

Lawter, A., Qafoku, N.P., Wang, G., Shao, H., Brown, C.F., 2016. Evaluating Impacts of CO2 Intrusion into an Unconsolidated Aquifer: I. Experimental Data. International Journal of Greenhouse Gas Control, 44: 323-333.

Lazareva, O., Druschel, G., Pichler, T., 2014. Understanding arsenic behavior in carbonate aquifers: Implications for aquifer storage adn recovery (ASR). Applied Geochemistry.

Leu, J.Y., Lin, Y.H., Chang, F.L., 2011. Conversion of CO2 into CH4 by methane-producing bacterium FJ10 under a pressurized condition. Chemical Engineering Research & Design, 89(9): 1879-1890.

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., 2010. Potential Impacts of Leakage from Deep CO_2 Geosequestration on Overlying Freshwater Aquifers. Environ. Sci. Technol., 44(23): 9225-9232.

Lu, J., Partin, J.W., Hovorka, S.D., Wong, C., 2010. Potential risks to freshwater resources as a result of leakage from CO_2 geological storage: a batch-reaction experiment. Environ. Earth Sci. , 60: 335-348.

Maclay, R.W., Small, T.A., 1994. Carbonate geology and hydrology of the Edwards Aquifer in the San Antonio area, Texas. OFR 83-537, U.S. Geological Survey.

McGrath, A.E., Upson, G.L., Caldwell, M.D., 2007. Evaluation and mitigation of landfill gas impacts on cadmium leaching from native soils. Ground Water Monitoring and Remediation, 27(4): 99-109.

Mickler, P.J., Yang, C.B., Scanlon, B.R., Reedy, R., Lu, J.M., 2013. Potential Impacts of CO2 Leakage on Groundwater Chemistry from Laboratory Batch Experiments and Field Push-pull Tests. Environmental Science & Technology, 47(18): 10694-10702.

Mohd Amin, S., Weiss, D.J., Blunt, M.J., 2014. Reactive transport modelling of geologic CO2 sequestration in saline aquifers: The influence of pure CO2 and of mixtures of CO2 with CH4 on the sealing capacity of cap rock at 37 °C and 100 bar. Chemical Geology, 367(0): 39-50.

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. Scientific Investigations Report 2010-5129, U.S. Geological Survey, Reston, Virginia.

Newmark, R.L., Friedmann, S.J., Carroll, S.A., 2010. Water Challenges for Geologic Carbon Capture and Sequestration. Environmental Management, 45(4): 651-661.

Nisi, B. et al., 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., Dahle, H.K., 2005. Semianalytical solution for CO2 leakage through an abandoned well. Environ. Sci. Technol., 39(2): 602-611.

Oldenburg, C.M., Doughty, C., 2011. Injection, Flow, and Mixing of CO2 in Porous Media with Residual Gas. Transport in Porous Media, 90(1): 201-218.

Oldenburg, C.M., Rinaldi, A.P., 2011. Buoyancy Effects on Upward Brine Displacement Caused by CO2 Injection. Transport in Porous Media, 87(2): 525-540.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) : a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water Resources Investigations Report 99-4259, U.S. Geological Survey, Washington, D.C.

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. et al., 2013. Geochemical Impacts of Leaking CO2 from Subsurface Storage Reservoirs to Unconfined and Confined Aquifers. PNNL-22420, PNNL-22420, Richland, WA.

RøeUtvik, T.I., 1999. Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. Chemosphere, 39: 2593–2606.

Romanak, K.D. et al., 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., 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.

Scherf, A.K. et al., 2011. Mobilisation of organic compounds from reservoir rocks through the injection of CO2 - Comparison of baseline characterization and laboratory experiments. Energy Procedia, 4: 4524-4531.

Skinner, L., 2003. CO[2] 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 CO_2 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.

Taggart, I., 2010. Extraction of Dissolved Methane in Brines by CO2 Injection: Implication for CO2 Sequestration. Spe Reservoir Evaluation & Engineering, 13(5): 791-804.

Tesoriero, A.J., Pankow, J.F., 1996. Solid solution partitioning of Sr2+, Ba2+, and Cd2+ to calcite. Geochimica Et Cosmochimica Acta, 60(6): 1053-1063.

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.

U.S. Environmental Protection Agency, 2009. Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, Unified Guidance. EPA 530/R-09-007, Washington, D.C.

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.

Viswanathan, H. et al., 2012. Developing a robust geochemical and reactive transport model to evaluate possible sources of arsenic at the CO2 sequestration natural analog site in Chimayo, New Mexico. International Journal of Greenhouse Gas Control, 10: 199-214.

Vong, C.Q. et al., 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. 10th International Conference on Greenhouse Gas Control Technologies, 4: 3171-3178.

Wang, G. et al., 2016. Geochemical Impacts of Leaking CO2 from Subsurface Storage Reservoirs to an Unconfined Oxidizing Carbonate Aquifer. International Journal of Greenhouse Gas Control, 44: 310-322.

Wang, S., Jaffe, P.R., 2004. Dissolution of a mineral phase in potable aquifers due to CO_2 releases from deep formations; effect of dissolution kinetics. Energy Convers. manage., 45(18-19): 2833-2848.

Wei, Y., Maroto-Valer, M., Steven, M.D., 2011. Environmental consequences of potential leaks of CO2 in soil. Energy Procedia 4: 3224−3230.

White, M.D. et al., 2012. STOMP Subsurface Transport Over Multiple Phases: STOMP-CO2 and STOMP-CO2e Guide: Version 1.0, Pacific Northwest National Laboratory, Richland, WA.

White, M.D., McGrail, B.P., 2005. STOMP, Subsurface Transport Over Multiple Phases, Version 1.0, Addendum: ECKEChem, Equilibrium-Conservation-Kinetic Equation Chemistry and Reactive Transport. PNN-15482, Pacific Northwest National Laboratory, Richland, Washington.

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.

Witter, A.E., Jones, A.D., 1999. Chemical characterization of organic constituents from sulfide-rich produced water using gas chromatography/mass spectrometry. Environ. Toxicol. Chem., 18: 1920-1926.

Wolery, T.W., Jarek, R.L., 2003. Software User's Manual, EQ3/6, Version 8.0, Sandia National Laboratories, Albuquerque, New Mexico.

Wunsch, A., Navarre-Sitchler, A.K., Moore, J., McCray, J.E., 2014. Metal release from limestones at high partial-pressures of CO2. Chemical Geology, 363: 40-55.

Wunsch, A., Navarre-Sitchler, A.K., Moore, J., Ricko, A., McCray, J.E., 2013. Metal release from dolomites at high partial-pressures of CO2. Applied Geochemistry, 38: 33-47.

Xiao, T. et al., 2016. Potential chemical impacts of CO2 leakage on underground source of drinking water assessed by quantitative risk analysis. International Journal of Greenhouse Gas Control, 50: 305-316.

Yang, C., Dai, Z., Romanak, K.D., Hovorka, S.D., Trevino, R.H., 2014. Inverse Modeling of Water-Rock-CO2 Batch Experiments: Potential Impacts on Groundwater Resources at Carbon Sequestration Sites. Environ Sci Technol, 48: 2798-2806.

Yang, C.B. et al., 2013. Single-well push-pull test for assessing potential impacts of CO2 leakage on groundwater quality in a shallow Gulf Coast aquifer in Cranfield, Mississippi. International Journal of Greenhouse Gas Control, 18: 375-387.

Yokoyama, Y., Tanaka, K., Takahashi, Y., 2012. Differences in the immobilization of arsenite and arsenate by calcite. Geochimica Et Cosmochimica Acta, 91: 202-219.

Zheng, L. 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(0): 202-217.

Zheng, L., Apps, J.A., Zhang, Y., Xu, T., Birkholzer, J.T., 2009. On mobilization of lead and arsenic in groundwater in response to CO_2 leakage from deep geological storage. Chemical Geology, 268(3-4): 281-297.

Zheng, L. et al., 2014. Reduced order models for prediction of groundwater quality impacts from CO 2 and brine leakage. Energy Procedia, 63: 4875-4883.

Zheng, L. et al., 2016. Evaluating Impacts of CO2 Intrusion into an Unconsolidated Aquifer: II. Modeling Results. International Journal of Greenhouse Gas Control, 44: 304-309.

Zheng, L. et al., 2013. On modeling the potential impacts of CO2 sequestration on shallow groundwater: Transport of organics and co-injected H2S by supercritical CO2 to shallow aquifers. International Journal of Greenhouse Gas Control, 14: 113-127.

Zheng, L., Spycher, N., Birkholzer, J., Xu, T., Apps, J., 2010. Modeling Studies on the Transport of Benzene and H_2S in CO_2-Water Systems, Lawrence Berkeley National Laboratory, Berkeley, California.

Zheng, L. et al., 2015. On the mobilization of metals by CO2 leakage into shallow aquifers: exploring release mechanisms by modeling field and laboratory experiments. Greenhouse Gases: Science and Technology, 5(4): 403-418.

Zhong, L., Cantrell, K.J., Bacon, D.H., Shewell, J., 2014a. Transport of organic contaminants mobilized from coal through sandstone overlying a geological carbon sequestration reservoir. International Journal of Greenhouse Gas Control, 21: 158-164.

Zhong, L.R., Cantrell, K., Mitroshkov, A., Shewell, J., 2014b. Mobilization and transport of organic compounds from reservoir rock and caprock in geological carbon sequestration sites. Environmental Earth Sciences, 71(9): 4261-4272.