Modeling the impact of carbon dioxide leakage into an unconfined, oxidizing carbonate aquifer

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ABSTRACT

Multiphase, reactive transport modeling was used to identify the mechanisms controlling trace metal release under elevated CO_2 conditions from a well-characterized carbonate aquifer. Modeling was conducted for both batch and column experiments. The column experiments resulted in higher trace metal concentrations because the rock to water ratio was higher. A kinetic desorption model fits the overall trends in release for seven trace metals observed in batch and column experiments exposing Edwards Aquifer material to elevated concentrations of CO_2. Observed and predicted trace metal concentrations are compared to groundwater concentrations from this aquifer to determine the potential for leaking CO_2 to adversely impact drinking water quality. Finally, a three-dimensional multiphase flow and reactive-transport simulation of CO_2 leakage from an abandoned wellbore into a generalized model of the shallow, unconfined portion of the aquifer is used to determine potential impacts on groundwater quality. As a measure of adverse impacts on groundwater quality, both the EPA's regulatory limits and the maximum trace metal concentration observed in the aquifer were used as threshold values. Results of the field-scale simulations indicate that CO_2 leakage into a carbonate aquifer is likely to cause decreases in pH and increases in TDS beyond observed ranges in the aquifer and beyond regulatory limits. However, trace metal concentrations are not predicted to exceed either the observed maximums or the regulatory limits.

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1. Introduction

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. Harvey et al. (2013) conducted a comprehensive review of the recently published literature regarding how elevated CO_2 levels may affect geochemical processes under low-temperature, low-pressure conditions characteristic of near-surface environments. Emphasis was placed on CO_2-induced effects on dissolution/precipitation and adsorption/desorption reactions, and consequences for the geochemistry of the vadose zone and potable aquifers. The review concluded that a significant amount of new scientific evidence suggests that CO_2 intrusion into potable aquifers or the vadose zone may have both beneficial and deleterious outcomes.

A number of modeling studies have focused on the potential for mobilization of toxic metals in groundwater due to acidification of the aquifers; many of these studies have focused on sandstone aquifers. For instance, Vong et al. (2011) modeled a glauconitic sandstone aquifer exposed to CO_2 over 10 years and predicted elevated Cd, Pb, and Zn concentrations due to acidification and dissolution of greenockite, galena, and sphalerite. Jacquemet et al. (2011) developed a similar model with SO_x and NO_x as impurities in the CO_2 gas stream and found increased aqueous Fe and Mn mineral dissolution. Wang and Jaffe (2004) modeled buffered and unbuffered aquifers exposed to CO_2 for 8 years and found increased Pb concentrations from acidic dissolution of galena. Zheng et al. (2009) modeled an Eastern Coastal Plain aquifer exposed to CO_2 for 100 years and predicted increased aqueous Pb and As due to galena and arsenian pyrite dissolution. A modeling study of the vadose zone exposed to CO_2 for up to 40 days by Altevogt and Jaffe (2005) predicted the potential mobilization of toxic metals

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due to acidification of the vadose zone pore fluids. Zheng et al. (2012) modeled CO_2 injection for 30 days into the shallow groundwater at the Zero Emission Research and Technology field site in Bozeman, Montana, and predicted increased dissolution of reactive Fe-bearing minerals and that calcite dissolution would result in increased solution concentrations of calcium and carbonate that would drive ion-exchange reactions in the sediment. Viswanathan et al. (2012) developed an inverse reactive-transport model to interpret As mobilization observed in a batch experiment with sedimentary samples collected from a shallow sandstone aquifer in New Mexico where CO_2 is actively upwelling and has been studied as a natural analog. Because these studies focused on sandstone aquifers, the effects of acidification are likely to be more severe than in a carbonate aquifer which can buffer pH changes due to CO_2 leakage.

One experimental study has included carbonate aquifers. Yang et al. (2014) performed inverse reactive-transport modeling of water–rock–CO_2 batch experiments for potable aquifers, three carbonate-poor and three carbonate-rich, from the Gulf Coast area and found that release of Ba, Mn, and Sr were likely regulated by mineral dissolution (Type I), and that As solubility was controlled by adsorption/desorption from clay (Type II). Also, a modeling study has focused on trace metal release from pure minerals, including calcite. Navarre-Sitchler et al. (2013) used reactive-transport modeling to predict the release of Pb from either galena or calcite solid solution and found that regardless of the Pb source, the Pb concentrations in solution remained below the maximum contaminant level (MCL) for Pb set by the U.S. Environmental Protection Agency (15 μg/L). However, the formation of aqueous complexes like PbCO3(aq) that would form under reducing conditions was not considered, which would significantly increase the solubility of galena and increase the total aqueous concentration of Pb. Also, the EPA's Class VI Rule requires groundwater geochemistry monitoring above the confining zone to detect changes in aqueous geochemistry resulting from fluid leakage out of the injection zone (40CFR 146.90(d)) where the results of groundwater monitoring may be compared against baseline geochemical data collected during site characterization to obtain evidence of fluid movement that may impact underground sources of drinking water (USDWs) (U.S. Environmental Protection Agency, 2012). Therefore the MCL is not the correct threshold for determining the impact of CO_2 leaks on groundwater. It is important to establish the baseline groundwater chemistry that captures the natural variability of trace metal concentrations in USDWs, and to look for changes greater than the natural variability with space and time (Last et al., 2013). Bacon et al. (2014) modeled trace metal release from a shallow carbonate aquifer in response to CO_2 leakage using equilibrium surface complexation reactions taken from the literature.

Experimental measurements are needed to identify the mechanisms controlling trace metal release from a particular aquifer material. Experimental work has largely focused on batch studies. Little and Jackson (2010) conducted a yearlong CO_2-nanopure water-sediment study with sediments from aquifers that overlay potential geologic carbon storage sites in the United States and found that aqueous concentrations of some species (Mn, Fe, Co, Ni, and Zn) increased, some (e.g., Mo) decreased, and others remained unaffected. Lu et al. (2010) exposed sediments from carbonate-poor and carbonate-rich potable aquifers in the U.S. Gulf Coast region to CO_2 for two weeks and observed that "Type I" cations that were controlled by mineral dissolution (Ca, Mg, Si, K, Sr, Mn, B, Zn) rapidly increased and reached stable concentrations and that "Type II" cations that were controlled by adsorption/desorption from clay (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) increased but then declined. Wei et al. (2011) exposed variably saturated soils to CO_2 at 25 bar for 3 days and observed that aqueous concentrations of some species increased (Mg, K, Al, V, Cr, Mn, Fe, Co, Cu, Rb, Sr, Ba, Pb, and U) and others (Zn and Cd) decreased. However, the mechanisms that control the release of elements into the aqueous phase are not currently well understood.

The objective of this paper is to use modeling to identify the mechanisms controlling trace metal release under elevated CO_2 conditions from a well-characterized carbonate aquifer, the shallow/urban unconfined portion of the Edwards aquifer near San Antonio, Texas, containing little clay, which is an USDW. Modeling was conducted for two experimental scenarios: batch experiments to simulate sudden, fast, and short-lived release of CO_2 as would occur in the case of well failure during injection, and column experiments to simulate more gradual leaks such as those occurring along undetected faults, fractures, or well linings. Observed and predicted trace metal concentrations are compared to groundwater from this aquifer to determine the potential for leaking CO_2 to adversely impact drinking water quality. Finally, a three-dimensional multiphase flow and reactive-transport simulation of CO_2 leakage from an abandoned wellbore into a generalized model of the shallow, unconfined portion of the Edwards Aquifer is used to determine potential impacts on groundwater quality. As a measure of adverse impacts on groundwater quality, we use both the EPA's MCL limits and the maximum trace metal concentration observed in the aquifer.

2. Methods

2.1. Aquifer data

The National Risk Assessment Partnership (NRAP) consists of five U.S. Department of Energy national laboratories collaborating to develop a framework for predicting the risks associated with carbon sequestration (https://edx.netl.doe.gov/nrap/). The NRAP Groundwater Protection Working Group chose Edwards Aquifer for study because it is a well-characterized carbonate aquifer. As

Table 1
Summary statistics and EPA primary drinking water standards for pH, TDS, and MCLs for trace metals in 90 groundwater samples from the shallow/urban unconfined portion of the Edwards Aquifer (Musgrove et al., 2010).

Measurement	Number of samples	Number of detections	Minimum	25th percentile	Median	75th percentile	Maximum	MCL
pH, standard units	90	90	6.28	6.8	6.87	6.92	7.29	6.5
TDS (mg/L)	90	90	201	312	329	360	456	500
Sb (μg/L)	87	3	<.05	<.2	<.30	<1	.06	6
As (μg/L)	87	54	<.9	<1	.27	.34	1.11	10
Ba (μg/L)	87	87	22.9	32.1	36.9	42.3	69.9	2000
Be (μg/L)	87	1	<.06	<.06	<.06	<1	.04	4
Cd (μg/L)	87	0	<.04	<.04	<.04	<1	<1	5
Cr (μg/L)	87	67	<.8	.20	.44	2.09	5.57	100
Cu (μg/L)	87	50	<.4	<.4	.33	1.04	57.3	1300
Pb (μg/L)	83	24	<.08	<.08	<1	.05	.15	15
Se (μg/L)	87	56	<.08	<1	.26	.35	1.4	50
Th (μg/L)	52	4	<.04	<.04	<.04	<.04	.05	2