Tracing CO₂ leakage into groundwater using carbon and strontium isotopes during a controlled CO₂ release field test

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Abstract

During a carbon sequestration field study to simulate the impact of CO₂ migration on shallow groundwater chemistry, the stable isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and dissolved strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) were evaluated as tracers. Dissolved CO₂ in groundwater was introduced using a closed-loop dipole-style well field situated in a shallow sand-dominated aquifer. Baseline $\delta^{13}\text{C}_{\text{DIC}}$ values, oxygen and hydrogen isotope ratios, and $^{87}\text{Sr}/^{86}\text{Sr}$ values of groundwater were established in four monitoring wells (MW-1 to 4) and one up-gradient background well (BG-1) prior to the introduction of dissolved CO₂. Baseline groundwater $\delta^{13}\text{C}_{\text{DIC-PDB}}$, oxygen ($\delta^{18}\text{O}_{\text{SMOW}}$) and hydrogen ($\delta\text{D}_{\text{SMOW}}$) stable isotope values averaged -17, -4.1 and -19.5 ‰, respectively. Groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ baseline values averaged 0.70840 at MW-3 and 0.70818 at MW-2. Arrival of the dissolved CO₂ plume at the monitoring wells is modeled using a 1-D analytical solution, and yields breakthrough curves with flow velocities that are consistent with prior numerical modeling estimates. The $\delta^{13}\text{C}_{\text{DIC-PDB}}$ rose to an average steady-state value of 0.16 ± 0.3 ‰ during the test; $\delta^{18}\text{O}$ and δD of water did not change from their baseline values. $^{87}\text{Sr}/^{86}\text{Sr}$ dropped sharply by 0.00022 at MW-3 and 0.00005 at MW-2 in the first two weeks after plume arrival at the wells, and then slowly increased toward baseline values, correlating with the behavior of dissolved Na, K, Ca, Sr and Si. Carbonate dissolution and desorption from organic matter and Fe-bearing phases at the low-pH plume front is the likely mechanism producing this behavior. The $\delta^{13}\text{C}_{\text{DIC}}$ and the $^{87}\text{Sr}/^{86}\text{Sr}$ of dissolved strontium served as excellent tracers of plume movement during this experiment.

Keywords: CO₂ sequestration, carbon isotopes, strontium isotopes, groundwater monitoring

1.0 Introduction

The ability to accurately detect leaks to shallow groundwater from deep geological carbon sequestration reservoirs is a critical component of any successful monitoring program, and necessary to move this technology from the demonstration to commercial scale. In addition to geophysical methods and groundwater monitoring of major or trace element chemistry, isotopic techniques are also proposed as sensitive methods to detect and quantify the extent of CO₂ and brine intrusion into shallow aquifers. Measured isotope ratios may also provide additional information on the source of the fluid and geochemical reactions with aquifer minerals and organic matter.

Studies on natural geological analog systems have shown that the stable isotope ratios of dissolved inorganic carbon, CO₂ and helium isotopes can be used to identify the presence and fate of migrating CO₂ in groundwater (e.g., Gilfillan et al., 2009; Gilfillan et al., 2011; Keating et al., 2010; Keating et al., 2014). However, most of these studies focus on the gradual increase and long-term risk of CO₂ intrusion into aquifers and do not fully inform strategies for early detection in a sequestration scenario. Field demonstrations of CO₂ sequestration allow studies that capture the critical period during and directly following CO₂ injection. For example, at the Weyburn demonstration site in Saskatchewan, Canada, carbon isotopes were used with success to quantify the dissolution and ionic trapping of CO₂ injected into a deep aquifer (Raistrick et al., 2006), and Sr isotopes monitored possible carbonate dissolution (Quattrocchi et al., 2006). The geochemical processes quantified in these studies are generally applicable to shallow groundwater, but they were focused primarily on the target sequestration reservoir at significantly higher temperature and pressure. Similarly, at the Frio site in Texas, USA, measured carbon and oxygen isotope ratios assisted in monitoring the movement of injected CO₂ into a deep reservoir as well as CO₂ migration into aquifers overlying the injection zone (Kharaka et al., 2009). While this study shows that these isotopes can detect the leakage of CO₂ above the reservoir, the monitoring took place at depths well below drinking water aquifers. In contrast, carbon isotopes were employed at the ZERT demonstration site in Montana, USA to monitor gas phase release of CO₂ in the shallow subsurface and to the atmosphere (Krevor et al., 2010). Additionally, trends in gas compositional ratios combined with stable isotopes have also been applied in vadose zone settings to detect potential leakage from deep sequestration reservoirs (Romanak et al., 2012). Although these near-surface techniques showed the ability to

identify leaking CO₂, they are not directly applicable to groundwater monitoring. A push-pull well test into a shallow aquifer (73 m) that introduced CO₂-charged groundwater showed that carbon isotope ratios in combination with other geochemical parameters can be used successfully to quantify mixing between groundwater and a potential CO₂ leak (Yang et al., 2013).

As part of a field-scale controlled CO₂ release test in shallow groundwater (Fig. 1), we tested the utility of carbon stable isotope ratios of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios) in groundwater to monitor the movement of a dissolved CO₂ plume at Southern Company Inc. Plant Daniel, Mississippi. Previous results from this test show that the introduction of dissolved CO₂ resulted in large increases in dissolved inorganic carbon, a drop in pH, and increases in major and trace elements at the monitoring wells as the plume migrated through the well field, toward PW-1 (Trautz et al., 2013). Elemental concentrations returned to near background conditions relatively quickly even though the dissolved CO₂ injection continued and the pH remained depressed. If the carbon stable isotope composition of this injected dissolved CO₂ differs from the background range in the aquifer, the $\delta^{13}\text{C}_{\text{DIC}}$ should serve as an excellent tracer of plume breakthrough at the monitoring wells as long as carbon isotope effects such as dissolution, reaction with substrate, or adsorption to substrate do not significantly change the $\delta^{13}\text{C}$ value of the injected CO₂ (e.g., Humez et al., 2014). Additionally, because the observed shifts in element concentrations included dissolved strontium, changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ may provide information on which aquifer phase(s) are releasing strontium into the groundwater. Based on these previous results and observations, the research questions that motivate this study include: (1) how effective are carbon isotope ratios as a tracer of dissolved CO₂ addition and movement in an aquifer and what magnitude of change from baseline values can be attributed to this carbon source? And (2) do strontium isotope ratios track fluid-rock reaction due to the addition of dissolved CO₂ and can they be combined with elemental analyses to identify which aquifer minerals are impacted?

Figure 1. Plan view and cross-section of the test site (modified from Trautz et al., 2013). BG-1 is projected onto cross-section line for reference. Groundwater flow was induced in the site by pumping from PW-1 and injection back into IW-1. Groundwater was monitored at MW-1 to 4 and upgradient background well BG-1.

2.0 Test Setting and Methods

2.1. Controlled injection experiment

The test site is a dipole-style well field that was installed into a ~6 m thick sand aquifer at a depth of ~50 m, confined above and below by clay horizons (Fig. 1). Wells included an injection and pumping well (IW-1, PW-1), four monitoring wells (MW-1 to 4), and one upgradient background well (BG-1). Groundwater was removed from PW-1 and reintroduced into IW-1 to induce a flow gradient through the monitoring well field. After a 2-month period of

pumping to establish steady-state flow and chemistry conditions, extracted groundwater was saturated with CO₂ to just below aquifer pressures and introduced at IW-1 starting on October 18, 2011. The injection of dissolved CO₂ and pumping of the well field were ended on March 23, 2012. Additional details of the test design, implementation and initial results are presented in Trautz et al. (2013)

To effectively identify isotopic shifts due to the breakthrough of the dissolved CO₂ plume at the monitoring wells, background stable isotope compositions were measured during active pumping. Although oxygen and hydrogen isotopes in water were not expected to shift due to the introduction of the dissolved CO₂ plume, these were measured to characterize variability in the groundwater composition due to induced flow by pumping. An up-gradient background well was also monitored prior to and during the test to establish the variability of background ranges of these isotopes. Sampling frequency during the CO₂ test was determined based on a combination of pumping tests, model calculations and a dissolved argon tracer test (Trautz et al., 2013).

2.2. Sample collection

For the injection test, groundwater that was pumped from PW-1 was equilibrated with CO₂ to just below aquifer saturation conditions (pCO₂ ~3.8 bar, 22°C, pH ~5) and introduced into IW-1 at ~50 m depth (Figure 1) (Trautz et al., 2013). Because aqueous samples were pumped to and collected at the surface, the impact of CO₂ degassing on the stable isotope composition of carbon was a concern. This was mitigated by collecting groundwater in 30 cm long by 0.95 cm O.D. annealed copper tubes sealed either with Swagelock® valves or refrigeration pinch-off clamps, similar to dissolved gas sampling methods for geothermal wells, hot springs and fumaroles (Giggenbach and Goguel, 1989; Hilton et al., 2002). These were collected at a backpressure of approximately 1.4 - 2 bar (20 - 30 psig) to ensure that CO₂ remained dissolved in the collected samples; bubble formation in the sample tubes could lead to subsequent errors in determining the carbon isotopic values. For dissolved metals and strontium isotopes, groundwater was filtered (0.45 µm) into 60 ml polyethylene (Nalgene®) bottles and field acidified to a pH<2 with trace-metal grade nitric acid.

2.3 Stable isotope analysis

Samples collected for stable isotope analysis were extracted from the 30 cm copper tubes into 20 ml gas-tight glass vials. Details of this extraction procedure are presented in Trautz et al. (2013). Aliquots of water were removed from these vials for subsequent stable isotope measurements at Los Alamos National Laboratory. Stable isotope ratios of dissolved inorganic carbon, oxygen and hydrogen in water were determined using standard methods by continuous flow isotope ratio mass spectrometry (CF-IRMS) on a GV Instruments Isoprime mass spectrometer coupled to a Multiflow peripheral instrument using CO₂-equilibration for carbon and oxygen and chromium reduction for hydrogen. Results are reported using standard delta notation in per mil (‰) (Sharp, 2006). $\delta^{13}\text{C}$ is reported versus PDB (Pee Dee Belemnite) with NBS-19 having a $\delta^{13}\text{C}$ value of 1.95‰, and $\delta^{18}\text{O}$ and δD are reported versus SMOW (Standard Mean Ocean Water) with SMOW having a $\delta^{18}\text{O}$ and δD value of 0‰. Standard deviations for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and δD measurements based on in-house and international standards were 0.13, 0.12 and 0.5 ‰ respectively.

2.4 Strontium isotope analysis

Strontium was separated from the ground water matrix and analyzed on a Thermo Neptune® multicollector ICP-MS (MC-ICP-MS) at the University of Pittsburgh following the procedure of Wall et al. (2013). An aliquot of groundwater containing approximately 2 µg of Sr was evaporated to dryness and redissolved in 8 N HNO₃. Separation of Sr from the other matrix elements was carried out using a vacuum box method with Sr Resin® (Eichrom) in a disposable polypropylene column; matrix elements were eluted with 8 N HNO₃, and a clean Sr cut eluted with H₂O. The separated Sr solution was collected in an acid-cleaned polypropylene centrifuge tube, diluted to 2% HNO₃, and the solution analyzed directly for $^{87}\text{Sr}/^{86}\text{Sr}$ on the MC-ICP-MS. Instrumental mass fractionation was corrected using an exponential law, normalizing to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. In addition, NIST Standard SRM 987 was run repeatedly with the unknown samples, and the final $^{87}\text{Sr}/^{86}\text{Sr}$ value of the sample reflects the offset from this standard over the period of the analysis. To allow comparison of data from this lab over long time periods, the data were normalized to a long-term SRM987 value of 0.710240. Estimated external reproducibility is ± 0.000025 . Maximum total procedural blanks ranged from 40 to 320 pg Sr (n= 5), resulting in a maximum blank/sample ratio of 0.00016, which is negligible.

3.0 Results

3.1 Baseline isotopic composition

3.1.1 Carbon, oxygen and hydrogen stable isotope compositions

Carbon, oxygen and hydrogen stable isotope ratios were measured at IW-1, BG-1, and MW-1, 3 and 4 during pumping prior to the CO₂ test start on October 18, 2011 to define baseline compositions during induced groundwater flow (*i.e.*, dynamic baseline) (Table 1 and S1, Figures 2 and 3). During this period, a short (3 – day) dissolved argon tracer test was conducted to refine the sampling frequency, and measurements during this test are not included in the background determination. The dynamic baseline values of $\delta^{18}\text{O}_{\text{SMOW}}$ and $\delta\text{D}_{\text{SMOW}}$ ranged from -4.4 to -3.8 ‰ and -21.8 to -17.2 ‰, respectively (Fig. 2), consistent with regional meteoric water (Kendall and Coplen, 2001). The carbon isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC-PDB}}$) measured prior to the start of the CO₂ test within the monitoring well field (MW-1 to 4) ranged from -17.6 to -15.2 ‰ (Table 1). At the up-gradient background well, BG-1, values spanned the same range from -17.5 to -15.2 ‰ for the entire experiment. These values are consistent with dissolved inorganic carbon that is derived from a terrestrial organic source (e.g., soil gas, sedimentary organic matter) (Sharp, 2006).

Table 1. $\delta^{13}\text{C}$ of dissolved inorganic carbon (‰ vs. PDB) at the monitoring wells prior and during the CO₂ experiments

Sampling Date	Monitoring Well				
	BG-1	MW-1	MW-2	MW-3	MW-4
8/31/11	-15.21				
9/1/11		-17.4	-16.96	-16.22	
9/7/11	-17.52		-17.58		-15.18
9/22/11					
9/28/11					
9/29/11		-17.6		-17.57	-17.32
10/19/11				-17.31	
10/21/11				-17.35	
10/24/11				-17.23	
10/26/11				-16.52	
10/28/11				-15.22	
10/31/11				-8.3	
11/2/11				-3.43	
11/3/11				0.46	
11/7/11				0.41	
11/9/11				-0.49	
11/9/11				0.61	

Sampling Date	Monitoring Well				
	BG-1	MW-1	MW-2	MW-3	MW-4
11/11/11				0.37	
11/14/11				0.65	
11/16/11				0.42	
11/18/11				0.9	
11/21/11				0.33	
11/23/11				0.72	
11/25/11				0.06	
11/28/11				-0.08	
11/30/11				-0.18	
12/2/11				-0.21	
12/5/11				-0.04	
12/7/11			-15.76	0.05	
12/14/11			-16.39	-0.33	
12/21/11			-15.93	-0.46	
12/28/11			-14.59	-0.6	
1/4/12			-7.91	0.3	
1/6/12		-14.92	-4.92		
1/9/12			-3.19		
1/11/12		-16.71	-3.06		
1/13/12		-16.69	-2.52		
1/16/12		-16.14	-0.92		
1/18/12		-16.72	-0.76		
1/20/12		-16.40	-0.28		
1/23/12		-15.7	-0.77		
1/25/12			-0.52		
1/28/12					-16.48
2/1/12		-15.61	-0.33		
2/1/12					
2/3/12		-15.08	0.18		
2/6/12		-14.34	0.06		
2/8/12		-13.68	-0.28		
2/10/12		-12.22	0.09		
2/13/12		-10.51	0.04		
2/15/12		-8.72	-0.17		
2/17/12		-7.51	-0.21		
2/22/12		-5.15	-0.3		
2/24/12		-3.92	-0.19		
2/27/12		-2.7	0.14		
2/29/12		-2.23	0.01		
3/2/12		-1.49			
3/5/12		-1.26	-0.32		
3/7/12		-1.06	0.07		
3/7/12		-1.16	0.21		
3/9/12		-0.68	-0.07		
3/9/12		-0.43	0.19		
3/12/12		-0.15	-0.22		
3/14/12		0.5	0.31		-15.85
3/15/12	-17.35			-0.13	
3/19/12		0.47	0.09		-15.75

Sampling Date	Monitoring Well				
	BG-1	MW-1	MW-2	MW-3	MW-4
3/21/12		0.7			
3/26/12		0.62	0.19		-15.47
3/29/12		0.64	-0.27		-14.45
3/30/12	-15.83			-0.29	
4/2/12		0.36	0.14		-14.25
4/5/12		-0.05	-0.26		-14.39
4/11/12	-16.23				-13.6
4/12/12		-0.62		-1.06	
4/16/12		-0.24	-0.62		-12.54
4/18/12	-16.19				
4/18/12		-0.54	-0.48	-1.01	-11.06
4/25/12		-0.92	-0.83	-1.26	-8.89
4/26/12	-16.26

Figure 2. Hydrogen and oxygen stable isotope compositions during the dynamic baseline period and during the CO₂ test. The global meteoric water line (GMWL) and a local meteoric water line (LMWL) are shown for reference (Craig, 1961; Kendall and Coplen, 2001).

3.1.2 Strontium isotope compositions

Strontium isotope measurements were made on samples from MW-3 and MW-2 to compare with carbon isotope variations during the CO₂ test. Dynamic baseline values of dissolved Sr and ⁸⁷Sr/⁸⁶Sr at MW-3 fell within the ranges of 0.100-0.130 mg/l and 0.70834-0.70846, respectively (Table 2, Figure 4). Baseline values prior to the start of the CO₂ experiment were not determined at MW-2, but pre-CO₂ breakthrough (based on δ¹³C_{DIC}, see section 3.2) fell within the ranges of 0.074-0.089 mg/l and 0.70818-0.70819 for dissolved Sr and

$^{87}\text{Sr}/^{86}\text{Sr}$, respectively (Table 2, Figure 5). These values are slightly lower than at MW-3, indicating some variability in the aquifer.

Table 2. Strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at MW-3 and MW-2 prior and during the CO_2 experiment

Date	Sr (mg/l)	$^{87}\text{Sr}/^{86}\text{Sr}^a$
MW-3		
08/09/2011	-	0.708461 ± 0.000008
08/15/2011	0.114	0.708409 ± 0.000007
08/17/2011	0.117	0.708342 ± 0.000007
08/19/2011	0.125	0.708465 ± 0.000008
08/21/2011	0.130	0.708395 ± 0.000005
08/27/2011	0.120	0.708335 ± 0.000007
10/19/2011	0.100	0.708389 ± 0.000006
10/24/2011	0.098	0.708325 ± 0.000006
10/26/2011	0.110	0.708334 ± 0.000006
11/04/2011	0.500	0.708242 ± 0.000008
11/11/2011	0.530	0.708167 ± 0.000008
11/14/2011	0.440	0.708171 ± 0.000007
11/14/2011 ^b	-	0.708166 ± 0.000008
11/21/2011	0.290	0.708186 ± 0.000009
11/23/2011	0.230	0.708167 ± 0.000007
11/25/2011	0.240	0.708201 ± 0.000008
11/30/2011	0.180	0.708218 ± 0.000005
12/02/2011	0.160	0.708170 ± 0.000005
12/07/2011	0.180	0.708204 ± 0.000009
12/21/2011	0.168	0.708334 ± 0.000008
12/28/2011	0.167	0.708406 ± 0.000007
01/04/2012	0.160	0.708338 ± 0.000009
MW-2		
12/07/2011	0.076	0.708190 ± 0.000007
12/14/2011	0.075	0.708188 ± 0.000008
12/21/2011	0.074	0.708179 ± 0.000007
12/28/2011	0.089	0.708191 ± 0.000007
01/04/2012	0.140	0.708130 ± 0.000006
01/06/2012	0.240	0.708148 ± 0.000006
01/09/2012	0.290	0.708140 ± 0.000007
01/11/2012	0.380	0.708143 ± 0.000009
01/13/2012	0.400	0.708136 ± 0.000007
01/16/2012	0.360	0.708136 ± 0.000006

^aSr isotope ratios normalized to SRM 987 = 0.710240; uncertainty shown is 2 S.E. of the individual run

^breplicate analysis

3.2 Isotopic results from CO₂ experiment

Dissolved CO₂ was introduced continuously for 157 days into IW-1 from October 18, 2011 until March 23, 2012 (Trautz et al., 2013). At this point the injection was terminated and groundwater pumping ceased. $\delta^{18}\text{O}$ and δD during the test are presented in figure 2 and are shown to overlap with the measured dynamic baseline values.

In contrast to the hydrogen and oxygen isotope values of water, $\delta^{13}\text{C}_{\text{DIC}}$ showed a strong response during the injection test. Complete breakthrough of the dissolved CO₂ plume was observed at MW-1, 2 and 3 prior to the cessation of the injection test (Figure 3). $\delta^{13}\text{C}_{\text{DIC}}$ values rose from average baseline values of $\sim -16\text{‰}$ to steady-state values of $0.16 \pm 0.30\text{‰}$ prior to injection termination. Samples collected for approximately one month after the end of the test (until the end of April) from MW-1, 2 and 3 gradually decrease in $\delta^{13}\text{C}$ by approximately 1‰ . Well MW-4, the most distal monitoring well to IW-1, did not show breakthrough of the dissolved CO₂ plume until after the injection and flow were terminated, and increased to -8.90‰ through the end of groundwater sampling (Figure 3). Figures 4 and 5 compare the strontium isotope ratios of the groundwater to the carbon isotope results (at MW-3 and MW-2) and selected major elements (MW-3 only) during the CO₂ experiment. Although MW-3 and MW-2 had different baseline $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, both showed a shift to lower ratios that correlated with sharp increases in the $\delta^{13}\text{C}$ values. At MW-3 Sr isotope values shift downward by 0.00022; at MW-2 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio dropped by 0.00005. Although these appear to be small shifts, they are in excess of the external reproducibility of 0.000025 and statistically significant ($p < 0.01$). Sampling for strontium isotopes at MW-2 was terminated prior to observing any shift back toward baseline values (Figure 5). At MW-3, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were observed to return to near baseline values after approximately one month, even though dissolved CO₂ was continuously introduced during this period and carbon isotope values remained at their maximum steady-state values (Figure 4A).

Figure 3 Carbon isotopic composition ($\delta^{13}\text{C}_{\text{DIC}}$) of the dissolved inorganic carbon during the dissolved CO_2 injection test. The dashed lines indicate the start and end of the dissolved CO_2 injection, respectively. Groundwater pumping and dissolved CO_2 injection ended on March 23, 2012. Well BG-1 is an up-gradient background well that is not impacted by the test. The gray curves are the results of analytical modeling (C/C_0 versus time) of the breakthrough of the dissolved CO_2 plume at each well (see text for details).

Figure 4. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of groundwater at MW-3. A) Strontium isotopes (external reproducibility ± 0.000025) compared to $\delta^{13}\text{C}_{\text{DIC}}$ results. Note that the drop in $^{87}\text{Sr}/^{86}\text{Sr}$ corresponds to rapid increase in carbon isotope values. B) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and dissolved Ca and Sr concentrations (note log scale) showing an increase in dissolved metals with the drop in $^{87}\text{Sr}/^{86}\text{Sr}$. C) Dissolved elemental mass ratios of Ca/Si, Na/Si and K/Si compared to $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The drop in Sr isotope ratios correlates with an increase in Ca/Si and a decrease in Na/Si and K/Si.

Figure 5. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) compared to $\delta^{13}\text{C}_{\text{DIC}}$ at MW-2. Note that the shift to lower strontium isotope ratios is correlated with the sharp rise in $\delta^{13}\text{C}_{\text{DIC}}$, interpreted as breakthrough of the dissolved CO_2 plume.

At well MW-3, increases in calcium and strontium concentrations during the experiment generally correlate with the shifts in both carbon and strontium isotopes, although the $^{87}\text{Sr}/^{86}\text{Sr}$ trend is less pronounced; sampling frequency for strontium isotopes was significantly smaller (Figure 4B). Calcium and strontium concentrations rose rapidly for a period of two weeks, followed by a gradual decrease to steady-state concentrations slightly higher than baseline. To explore what might be controlling the shift in groundwater strontium isotopes (see section 4), Figure 4C compares $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to mass ratios of dissolved sodium, potassium and calcium relative to dissolved silica. These elemental ratios show similar pulse shapes as the calcium and strontium concentrations, with an early rapid change correlating to carbon and strontium isotope shifts, followed by a more gradual shift back toward baseline values after approximately 2 weeks. It is important to note that dissolved silica (not shown) also shows a pulse with a sharp increase in concentration followed by slower drop. The Ca/Si ratio increases to values statistically different from baseline ($p < 0.01$), whereas both the Na/Si and K/Si ratios show statistically significant ($p < 0.01$ and $p < 0.05$, respectively) decreases with respect to baseline. None of these ratios were observed to return completely to dynamic baseline values during the experiment.

4.0 Discussion

4.1 Carbon stable isotope ratios

The observed significant shift in the $\delta^{13}\text{C}_{\text{DIC}}$ at each monitoring well from baseline values of approximately -17 ‰ to higher values is interpreted as detection of breakthrough of the dissolved CO_2 plume (Figure 3). Based on these results, the dissolved CO_2 plume arrived first at MW-3, the nearest monitoring well, eight days after the start of the dissolved CO_2 introduction. This is consistent with the ~10 day arrival time observed during the dissolved argon test (Trautz et al., 2013) used to refine the sampling frequency during the CO_2 experiment. Plume arrival was detected at MW-2 after 71 days, MW-1 after 108 days, and at MW-4 on day 162, all consistent with their relative distance from the injection well. Numerical modeling estimates of the pH field after 120 days indicated that the plume should have just reached MW-1 and have fully broken through at MW-3 and MW-2 (Fig. 6 of Trautz et al., 2013). These results are consistent with the $\delta^{13}\text{C}$ measurements showing plume arrival at MW-1 after ~108 days (Figure 3).

4.2 Breakthrough curve evaluation

To further evaluate the $\delta^{13}\text{C}$ breakthrough curves, plume results from the field experiment are fitted with a simple 1-dimensional analytical solution to a coupled advection dispersion equation. Given the scale of the reservoir (6 m thick saturated zone), the horizontal distances between the injection well and monitoring wells (4.6 to 20 meters), and the time scale of the experiment (up to 200 days), it is likely that lateral and vertical displacement of CO_2 saturated water occurred. However, for the purposes of this test, which is to interpret carbon isotope results as a means to trace a CO_2 plume, the results from a 1-dimensional model are sufficient.

Concentration is evaluated for values of x (distance between the injection well and monitoring well) and t (time since injection) using an analytical solution to the mass transport differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

The CO_2 injection experiment was designed as a Dirichlet (first type) step function with the following boundary conditions: $C(0,t)=0$ $t < 0$, $C(0,t)=C_0$ $t \geq 0$, and $C(\infty,t)=0$ for all t . An

analytical solution to Equation 1 (Ogata, 1970; van Genuchten and Alves, 1982) with the listed boundary conditions is:

$$C(x, t) = \frac{1}{2} C_o \cdot \operatorname{erfc} \left[\frac{x-V \cdot t}{2\sqrt{D \cdot t}} \right] + \exp \left[\frac{V \cdot x}{D} \right] \cdot \operatorname{erfc} \left[\frac{x+V \cdot t}{2\sqrt{D \cdot t}} \right] \quad (2)$$

Mean flow velocity (v) and dispersion coefficient (D) are solved for distance (x) between injection well and monitoring well, measured concentration C(x,t), and time (t) using a nonlinear least squares parameter optimization method in the computer software package STANMOD CXFIT (Šimůnek et al., 1999). A deterministic 1-dimensional solution for resident concentration (first-type inlet) with a constant initial concentration was calculated.

Here, concentration was not measured directly; rather, the carbon isotope ratio of dissolved inorganic carbon (DIC) was measured. We use these isotope ratios to calculate the mole fraction of the CO₂-saturated injection fluid in each samples using:

$$\delta^{13}\text{C}_{\text{measured}} = \delta^{13}\text{C}_{\text{baseline}}(X-1) + \delta^{13}\text{C}_{\text{injected}}(X) \quad (3)$$

where X is the fraction of the injected fluid, $\delta^{13}\text{C}_{\text{measured}}$ is the ratio measure at time (t) at a monitoring well, $\delta^{13}\text{C}_{\text{injected}}$ is estimated as 0.16 ‰, which is the average carbon isotope ratio observed at MW-3 after complete plume breakthrough (Figure 3), and $\delta^{13}\text{C}_{\text{baseline}}$ was approximately -17 ‰ at all wells prior to the start of the experiment. Rearranged, this becomes:

$$X = (\delta^{13}\text{C}_{\text{measured}} + \delta^{13}\text{C}_{\text{baseline}}) / (\delta^{13}\text{C}_{\text{baseline}} + \delta^{13}\text{C}_{\text{injected}}) \quad (4)$$

Cast in the terms of equation (2), $X = C/C_o$, where 0 equates to baseline conditions and 1 represents complete breakthrough of the injected fluid.

Figure 3 also shows the analytical solution for each optimized breakthrough curve for each monitoring well dataset using STANMOD CXFIT (Šimůnek, et al., 1999). The decreased concentration tailing behavior observed after the termination of the experiment (Figure 3, after March 26, 2012) cannot be addressed using this model because it does not satisfy the boundary condition $C(0,t)=C_o$ $t \geq 0$. Therefore, the proposed model only includes data collected until March

26, 2012. The complete collected dataset is illustrated, however. Estimated groundwater seepage velocities and dispersion coefficients for MW-1, 2 and 4 ranged from 0.10 – 0.16 m/d and $1.2 \cdot 10^{-7}$ to $1.46 \cdot 10^{-7}$ m²/s, respectively. The nearest well to the injection, MW-3, differs and has a higher flow velocity and diffusion coefficient of ~0.34 m/d and $\sim 2.0 \cdot 10^{-7}$ m²/s, respectively. Pre-experiment pumping tests also identified a higher groundwater flow rate at MW-3; however, the estimated rate here is a factor of 2 larger. A likely reason for the differences in plume arrival proximal to the injection well is the effect of heterogeneity and the potential for fast paths to develop near the injection well. Our analysis of these breakthrough curves assumes a homogenous media. Vertical variability in electrical resistivity identified using cross-well measurements during this experiment were interpreted as variability in plume shape and concentration during breakthrough due to formation heterogeneity (Dafflon et al., 2013). Additional uncertainty exists in our estimates of seepage velocities and dispersion because we used a 1-D solution assuming parallel streamlines like a column test. Due to streamline arcs created in a two-well tracer test such as this experiment, a 2-D (e.g., Grove and Beetem, 1971) or 3-D solution would provide more certain results; however, this level of analysis is beyond the scope of this paper. We feel that the simple analysis presented here matches plume arrival and breakthrough behavior satisfactorily as tracked by carbon isotope ratios.

4.3 CO₂ source evaluation

In addition to clearly recording plume breakthrough behavior in the well field, $\delta^{13}\text{C}_{\text{DIC}}$ can also be used to gain insight on the nature of the dissolved CO₂ that was introduced into the aquifer. The pre-injection dissolved inorganic carbon values measured in the aquifer during pumping (dynamic baseline) was on the order of 6.4 mM (Trautz et al., 2013). The calculated maximum dissolved inorganic carbon in MW-3 was ~132 mM after complete breakthrough, tracked by a steady-state groundwater pH of ~5 (Trautz et al., 2013). Total dissolved carbon concentration was calculated in PHREEQC (Parkhurst and Appelo, 1999) at aquifer conditions using the measured groundwater major element chemistry, aquifer temperature, bicarbonate alkalinity and *in situ* pH (pH=5) from MW-3 (following methods in Newell et al., 2008). Calculation of this total dissolved carbon is necessary because the measured bicarbonate alkalinity of the groundwater does not account for significant contribution of carbonic acid (H₂CO₃) at low pH (Drever, 1997). A simple mass balance approach using these dissolved

carbon concentrations and the associated $\delta^{13}\text{C}$ measured at baseline and breakthrough conditions can be used to estimate the carbon isotope composition of the CO_2 used for the experiment based on the following equations (Sharp, 2006):

$$\delta^{13}\text{C}_{\text{Total}} = \delta^{13}\text{C}_{\text{baseline}}(X) + \delta^{13}\text{C}_{\text{CO}_2}(1-X) \quad (5)$$

Rearranged to:

$$\delta^{13}\text{C}_{\text{CO}_2} = [\delta^{13}\text{C}_{\text{Total}} - \delta^{13}\text{C}_{\text{baseline}}(X)]/(1-X) \quad (6)$$

Where X represents the mole fraction of total inorganic carbon contributed from the baseline concentration of DIC. Equation 6 is identical in form to equation (3); however, here we are calculating the carbon isotope composition of the CO_2 source that was used to create the injection fluid considered previously. While we were not able to measure the isotopic composition of the injected CO_2 used in the experiment, the calculated value based on equation (6) is $+1.03 \pm 0.30$ ‰, using the observed $\delta^{13}\text{C}_{\text{baseline}}$ of -17.0 ‰ and the $\delta^{13}\text{C}_{\text{Total}}$ of 0.16 ± 0.30 ‰ at steady state. This calculation assumes the sand aquifer acted as a closed system with no degassing driving Rayleigh fractionation of carbon isotopes (e.g., Gilfillan et al., 2009), and that reactions involving the dissolution of carbonate minerals or oxidation of organic carbon had negligible impacts on the carbon isotope composition. Because this aquifer is confined between thick clays and not in communication with the atmosphere in the study area (Figure 1) and carbonate cements are not observed and are only inferred as a trace component (TIC $<0.01\%$) (Trautz et al., 2013), these assumptions are likely to be valid. Trautz et al. (2013) reported low organic content for the bulk of the aquifer material (sand with a TOC of $<0.01\%$), with minor thin laminations containing up to 2.4% TOC. Thus, it is unlikely that passage of the dissolved CO_2 plume could have oxidized enough organic carbon to measurably alter the carbon isotopic composition of the groundwater.

4.4 Strontium isotope ratios

Based on their correlation with carbon isotope and major elements trends presented in Figures 4 and 5, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also track the breakthrough of the dissolved CO_2 plume. Trautz et al. (2013) reported that the shifts (pulses) in major elements correlated with the drop in pH and increase in dissolved CO_2 associated with plume breakthrough at the wells. While we were not

able to characterize the strontium isotope ratios of strontium-bearing phases in the aquifer (*e.g.*, feldspars, carbonates), we can use the behavior of selected elemental ratios to evaluate possible causes of the shift in isotopic ratios observed. Specifically, Na/Si and K/Si are used to track potential dissolution of sodium and potassium bearing feldspars or clays (present in the aquifer), and Ca/Si to track dissolution of calcium-bearing phases. In the aquifer calcium is present in organic matter and Fe-bearing phases (illite and Fe-hydroxides) and trace carbonate cements (Trautz et al., 2013). The drop in K/Si at MW-3 with plume arrival is not consistent with K-feldspar dissolution, which would raise the ratio, but rather the mobilization of silica. The drop in Na/Si is consistent with dissolution of Na-plagioclase (albite). However, albite is more likely to alter to clays and this would raise the Na/Si ratio (Na is mobilized, Si is not). Also, dissolved sodium and potassium concentrations show only small increases during plume arrival, whereas dissolved silica increases by a factor of 4. These results are most consistent with dissolution of amorphous silica due to the drop in pH and only minor mobilization of Na and K from other mineral phases. The large increase in calcium (4-5X) and associated increase in Ca/Si is most consistent with dissolution of carbonate cement and calcium desorbing from Fe-bearing phases (Fe-hydroxides, Fe-illite) or organic compounds. Strontium substitution for calcium in trace amounts of carbonate cement and the observed presence of strontium in organic matter and Fe-bearing phases (Trautz et al., 2013) would result in strontium also being released during dissolution. The $^{87}\text{Sr}/^{86}\text{Sr}$ of this released strontium is lower than the dissolved strontium present in the groundwater, causing the shift to lower values in MW-3 and MW-2, which argues for the carbonate dissolution as the mechanism. Adsorbed strontium on organic matter or iron-bearing phases are likely to have the same isotope ratios as the dissolved strontium in the groundwater and would not cause the observed shift. Interestingly, the baseline $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the groundwaters collected at MW-3 and MW-2 are slightly different from each other despite the proximity of the wells, but the downward isotopic shift observed at each well due to plume arrival is consistent.

Strontium isotopes provide further support for the hypothesis suggested by Trautz et al. (2013) that low pH conditions at the front of the dissolved CO_2 plume promoted mobilization of elements (*e.g.*, Ca and Sr) due to rapid desorption and dissolution of mineral phases (*i.e.*, carbonate). Following this, the drop in these elemental concentrations and increase in $^{87}\text{Sr}/^{86}\text{Sr}$ over a period of two weeks (Fig. 4) was caused by mixing with groundwater that had passed

through aquifer materials depleted in mobile elements by the CO₂ plume front. Figure 6 shows a mixing diagram in which the ⁸⁷Sr/⁸⁶Sr ratio is plotted against the inverse of the Sr concentration for MW-2 and 3. Linear regression of these data indicates that mixing of groundwater with a low Sr (high 1/Sr) and high ⁸⁷Sr/⁸⁶Sr with groundwater containing higher Sr (lower 1/Sr) and lower ⁸⁷Sr/⁸⁶Sr can explain 55 – 80% of the observed variability in MW-3 and MW-2, respectively. Higher strontium content, lower ⁸⁷Sr/⁸⁶Sr ratio end members (e.g., carbonate minerals, iron oxyhydroxides, organic matter) in each well correlate with the pulse created by breakthrough of the low pH CO₂ plume that resulted in dissolution and desorption, releasing strontium to the groundwater. Knowledge of the end member Sr isotopic compositions would allow quantification of the contribution of each of these processes. As of the end of the sampling campaign, the groundwater ⁸⁷Sr/⁸⁶Sr ratios, dissolved concentrations of calcium and strontium, and elemental ratios had not returned to baseline values (Figure 5). Longer term monitoring is necessary to determine if pre-experiment base line conditions will be reestablished or if this change represents a long-term impact.

Figure 6. Mixing diagram showing strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) versus 1/Sr concentration (L/mg) from MW-2 and MW-3. Linear regression for each well is shown with associated R².

5.0 Conclusions

Effective groundwater monitoring above geological carbon sequestration reservoirs to identify leaks and prevent degradation of drinking water quality will require a multidisciplinary approach. Given the large set of geochemical and geophysical tools available, technique

demonstration is necessary to identify the most cost-effective and practical method for a given monitoring scenario. In this study we explored the utility of combining a multiple isotope approach with standard groundwater geochemistry to rapidly detect the presence of a dissolved CO₂ plume in a shallow confined aquifer, track its effects on groundwater geochemistry, and determine relevant water-rock interactions.

During this field experiment, the carbon stable isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) served as an excellent tracer of the plume movement, producing classic breakthrough curves. In addition to carbon isotope ratios, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of dissolved strontium in the groundwater also detected plume arrival but for different reasons. The dissolution of CO₂ into the aquifer altered the dissolved inorganic pool but did not directly change the strontium content. However, the associated drop in pH resulted in carbonate mineral dissolution (and possibly desorption from organic matter and Fe-bearing phases), which in turn altered the strontium geochemistry. However, similar to other dissolved elements, the shift in $^{87}\text{Sr}/^{86}\text{Sr}$ did not persist, presumably because of depletion of carbonate minerals as the dissolution front passed through the aquifer and was replenished by groundwater. In terms of detecting and monitoring CO₂ leakage into shallow aquifers, several conclusions can be drawn from this experiment:

- Sampling and analysis for carbon stable isotopes in most groundwater systems is relatively straightforward and cost-competitive compared to other geochemical methods such as major and trace element analysis. It is important to minimize degassing and properly collect and preserve groundwater samples using the methods presented here or other published methodologies (*e.g.*, USGS, 2006) prior to analysis. Extensive degassing or post-collection biological degradation can introduce uncertainty into the interpretation of carbon stable isotopes.
- Baseline characterization of the tracers of interest in monitored groundwater is necessary. For carbon isotope ratios to work as a tracer, the variability in isotopic composition of the groundwater must be known, the composition and variability of the injected CO₂ must be known, and these compositions need to be different enough to be able to identify significant changes in the groundwater composition. We recognize that the concept of ‘baseline’ can be difficult to define, as groundwater geochemistry may change through time due to natural and other anthropogenic processes other than sequestration activities.

Thus, it is also important to know other contributing sources of dissolved carbon in the geologic column.

- Utilization of additional tracers will build confidence in a monitoring program. In this work we explored the utility of strontium isotopes. Whereas carbon isotopes in groundwater are directly influenced by the addition of CO₂, strontium isotopes primarily track dissolution of carbonate cements related to the plume passage. In this study, this was a transient process, but informative for understanding processes that may release trace elements that impact water quality. In addition, mineral dissolution can result in porosity and permeability changes that could affect migration pathways and speed. In a scenario where brine intrusion via displacement by CO₂ is potentially significant, strontium isotopes could be a powerful tracer (e.g., Chapman et al., 2012). Although significantly more expensive than carbon stable isotopes, the ability to rapidly separate and measure strontium isotopes by MC-ICPMS (Wall et al., 2013) has increased the accessibility of this tracer for a monitoring program.

On the whole, carbon isotopes did a better job of detecting and characterizing the dissolved CO₂ plume than alkalinity and major element chemistry that showed initial increases in response to arrival of the CO₂ plume, but then quickly dropped back toward baseline conditions. Thus in a monitoring situation, a leak could be missed if relying on these constituents alone. The carbon isotopic composition continued to reflect the impact of the dissolved CO₂. Groundwater pH also was effective (Trautz et al., 2013), but required either downhole pH measurements or in-line measurement at the surface to prevent the large errors introduced by degassing. Additionally, carbon isotopes can provide more information than pH alone. In this study, the injected CO₂ had a distinctly different composition than the groundwater, and a simple mass balance approach was applied to calculate the approximate composition of the injected CO₂. In aquifers that contain a more reactive matrix (i.e., significant amounts of carbonate minerals), then reaction with the matrix may impart another mixing component that could be potentially constrained using the combined measurement of carbon and strontium isotopes.

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7.0 References Cited

- Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., Edenhorn, H.M., 2012. Geochemical and strontium isotope characterization of produced waters from Marcellus Shale gas extraction. *Environmental Science & Technology* 46, 3545-3553.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133.
- Dafflon, B., Wu, Y., Hubbard, S.S., Birkholzer, J., Daley, T.M., Pugh, J., Peterson, J.E., Trautz, R.C., 2013. Monitoring CO₂ intrusion and associated geochemical transformations in a shallow groundwater system using complex electrical methods. *Environmental Science & Technology* 47, 314-321.
- Drever, 1997. *The Geochemistry of Natural Waters*, 3rd ed. Prentice Hall, Upper Saddle River.
- Giggenbach, W.F., Goguel, R.L., 1989. Methods for the collection and analysis of geothermal and volcanic water and gas samples. Department of Scientific and Industrial Research, Chemistry Division, Petone, New Zealand.
- Gilfillan, S.M.V., Sherwood Lollar, B., Holland, G., Blagburn, D., Stevens, S., Schoell, M., Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G., Ballentine, C.J., 2009. Solubility trapping in formation water as dominant CO₂ sink in natural gas fields. *Nature* 458, 614-617.
- Gilfillan, S.M.V., Wilkinson, M., Haszeldine, R.S., Shipton, Z.K., Nelson, S.T., Poreda, R.J., 2011. He and Ne as tracers of natural CO₂ migration up a fault from a deep reservoir. *International Journal of Greenhouse Gas Control* 5, 1507-1516.
- Grove, D.B., Beetem, W.A., 1971. Porosity and dispersion constant calculations for a fractured carbonate aquifer using the two well tracer method. *Water Resources Research* 7, 128-134.
- Hilton, D., Fischer, T.P., Marty, B., 2002. Noble gases and volatile recycling at subduction zones, in: Porcelli, D., Ballentine, C.J., Weiler, R. (Eds.), *Reviews in Mineralogy & Geochemistry - Noble Gases in Geochemistry and Cosmochemistry*. Mineralogical Society of America, Washington D.C., pp. 319-370.

504 Humez, P., Lions, J., Négrel, P., Lagneau, V., 2014. CO₂ intrusion in freshwater aquifers:
 505 Review of geochemical tracers and monitoring tools, classical uses and innovative approaches.
 506 Applied Geochemistry 46, 95-108.

507 Keating, E.H., Fessenden, J., Kanjorski, N., Koning, D.J., Pawar, R., 2010. The impact of CO₂
 508 on shallow groundwater chemistry: observations at a natural analog site and implications for
 509 carbon sequestration. Environ Earth Sci doi: 10.1007/s12665-009-0192-4, 521-536.

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

513 Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river water across
 514 the United States. Hydrologic Processes 15, 1363-1393.

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

518 Krevor, S., Perrin, J.-C., Esposito, A., Rella, C., Benson, S., 2010. Rapid detection and
 519 characterization of surface CO₂ leakage through the real-time measurement of $\delta^{13}\text{C}$ signatures in
 520 CO₂ flux from the ground. International Journal of Greenhouse Gas Control 4, 811-815.

521 Newell, D.L., Kaszuba, J.P., Viswanathan, H.S., Pawar, R.J., Carpenter, T., 2008. Significance
 522 of carbonate buffers in natural waters reacting with supercritical CO₂ - implications for
 523 Monitoring, Measuring and Verification (MMV) of geological carbon sequestration.
 524 Geophysical Research Letters 35, L23403, doi: 10.1029/2008GL035615.

525 Ogata, A., 1970. Theory of dispersion in a granular medium. U.S. Geological Survey
 526 Professional Paper 411-I, 34 p.

527 Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)-A computer
 528 program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical
 529 calculations. USGS Water-Resources Investigations Report 99-4259, 310.

530 Quattrocchi, F., Barbieri, M., Bencini, R., Cinti, D., Durocher, K., Galli, G., Pizzino, L.,
 531 Shevalier, M., Voltattorni, N., 2006. Strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) chemistry in produced oil field
 532 waters: The IEA CO₂ monitoring and storage project, in: Lombardi, S. (Ed.), *Advances in the*
 533 *Geological Storage of Carbon Dioxide*. Springer, Netherlands, pp. 243-259.

534 Raistrick, M., Mayer, B., Shevalier, M., Perez, R.J., Hutcheon, I., Perkins, E.H., Gunter, B.,
 535 2006. Using chemical and isotopic data to quantify ionic trapping of injected carbon dioxide in
 536 oil field brines. *Environmental Science and Technology* 40, 6744-6749.

537 Romanak, K.D., Bennet, P.C., Yang, C., Hovorka, S.D., 2012. Process-based approach to CO₂
 538 leakage detection by vadose zone gas monitoring at geologic CO₂ storage sites. *Geophysical*
 539 *Research Letters* 39, L15405.

540 Sharp, Z.D., 2006. *Principles of Stable Isotope Geochemistry*. Pearson/Prentice Hall, Upper
 541 Saddle River, N.J.

542 Šimůnek, J., van Genuchten, M.T., Šejna, M., Toride, N., Leij, F.J., 1999. The STANMOD
 543 computer software for evaluating solute transport in porous media using analytical solutions of
 544 convection-dispersion equation, Versions 1.0 and 2.0, IGWMC-TPS-71. International Ground
 545 Water Modeling Center, Colorado School of Mines, Golden, Colorado.

546 Trautz, R.C., Pugh, J.D., Varadharajan, C., Zheng, L., Bianchi, M., Nico, P.S., Spycher, N.F.,
 547 Newell, D.L., Esposito, R.A., Wu, Y., Dafflon, B., Hubbard, S.S., Birkholzer, J.T., 2013. Effect
 548 of Dissolved CO₂ on a Shallow Groundwater System: A Controlled Release Field Experiment.
 549 *Environmental Science & Technology* 47, 298-305.

550 USGS, 2006. National field manual for the collection of water-quality data, U.S. Geological
 551 Survey Techniques of Water-Resources Investigations: Book 9, A1-A9. USGS.

552 van Genuchten, M.T., Alves, W.J., 1982. Analytical Solutions of the One-Dimensional
 553 Convective-Dispersive Solute Transport Equation, Technical Bulletin 1661. United States
 554 Department of Agriculture, Agricultural Research Service.

555 Wall, A.J., Capo, R.C., Stewart, B.W., Phan, T.T., Jain, J.C., Hakala, J.A., Guthrie, G.D., 2013.
556 High throughput method for Sr extraction from variable matrix waters and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope
557 ratios by MC-ICP-MS. Journal of Analytical Atomic Spectrometry 28, 1338-1344.

558 Yang, C., Mickler, P.J., Reedy, R., Scanlon, B.R., Romanak, K.D., Nicot, J.-P., Hovorka, S.D.,
559 Trevino, R.H., Larson, T., 2013. Single-well push-pull test for assessing potential impacts of
560 CO₂ leakage on groundwater quality in a shallow Gulf Coast aquifer in Cranfield, Mississippi.
561 International Journal of Greenhouse Gas Control 18, 375-387.

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563