

Insights into interconnections between the shallow and deep systems from a natural CO₂ reservoir near Springerville, Arizona



Elizabeth Keating^{a,*}, Dennis Newell^b, David Dempsey^a, Rajesh Pawar^a

^a Los Alamos National Laboratory, United States

^b Utah State University, United States

ARTICLE INFO

Article history:

Received 9 September 2013

Received in revised form 19 February 2014

Accepted 20 March 2014

Keywords:

Groundwater protection

Faults

Natural analog

ABSTRACT

If carbon dioxide (CO₂) sequestration into deep geologic reservoirs is to be accepted by the public and environmental regulators, the possibility of upward leakage into shallow groundwater should be acknowledged and those processes well-understood. Studies of natural CO₂ reservoirs and their connection (or lack thereof) with the shallow subsurface is one way to explore these issues. A natural reservoir near Springerville, Arizona has leaked CO₂ to the surface along a fault zone for thousands of years, creating large travertine deposits. In recent times, the CO₂ leak rates have declined significantly yet the shallow aquifer is still highly enriched in CO₂. In this study, using water level data and simulations we demonstrate that the fault zone likely provides hydrologic communication between the shallow aquifer and the deeper reservoir. It is reasonable to assume, therefore, that the source of the CO₂ in wells completed within the fault zone is the deeper CO₂ reservoir. We present water chemistry data to demonstrate the geochemical impact of this CO₂ on shallow groundwater quality. Interestingly, arsenic concentrations are elevated, but other trace metals concentrations are not. Arsenic and chloride concentrations co-vary, suggesting perhaps an external source of both elements rather than an in situ release of As due to CO₂ attack on shallow aquifer sediments. Observations at this site demonstrate that hydraulic communications between shallow and deep layers and upward CO₂ migration does not preclude long-term viability of a substantial CO₂ reservoir at depth. We present multi-phase flow simulations to illustrate possible mechanisms trapping the CO₂ at depth. Collectively, these analyses show that some degree of upward CO₂ leakage may not be necessarily incompatible with the overarching goals of sequestering CO₂ and protecting shallow groundwater.

Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

Injection of anthropogenic carbon dioxide (CO₂) into the subsurface has been suggested as an important component of a multi-faceted effort to reduce greenhouse gases (DOE). Carbon dioxide has been successfully injected into depleted oil fields for decades, but demonstrations of successful CO₂ injection into other deep reservoirs, such as saline aquifers, are fairly few and all relatively recent (Korbol and Kaddour, 1995; Preisig and Prevost, 2011; Hovorka et al., 2006, 2011). Of course it is not sufficient merely to inject the CO₂; a successful sequestration project will have to demonstrate that almost all of the CO₂ stays in the deep reservoir and, if any leaks upward, that it does not negatively impact shallow drinking water resources. This paper uses observations at a

natural CO₂ reservoir near Springerville, Arizona to shed light on both long-term storage and upward leakage.

Natural-occurring gas reservoirs are distributed throughout the world and have been exploited primarily for methane, noble gases, and carbon dioxide. The fact that these reservoirs have existed for millions of years has been used to argue that injected CO₂ can be stable in deep reservoirs and that caprocks can maintain their integrity for long periods of time. Some natural reservoirs, however, do leak gases to the surface. Understanding the mechanisms of leakage and the impact of the leakage on shallow groundwater resources using a 'leaky' natural reservoir near Springerville, Arizona is the focus of this study. Additionally, we address the question 'how is it possible that a substantial volume of gas-phase CO₂ can be stored underground in the presence of a large leakage pathway?'

Previous studies of the impact of CO₂ sequestration on shallow groundwater resources have focused on two issues: (1) CO₂ intrusion into the shallow aquifer, which may lower groundwater pH and mobilize trace metals (Little and Jackson, 2010; Kharaka et al.,

* Corresponding author. Tel.: +1 5056656714.
E-mail address: ekeating@lanl.gov (E. Keating).

2010), and/or (2) brine intrusion, which would introduce salts and trace metals into the groundwater (Keating et al., 2010). The leakage pathway could be an abandoned well, a fault, or a localized caprock breach. Leakage pathways could be natural or 'activated' by overpressurization due to injection. Simulation and natural analog studies have addressed the physical mechanism of brine intrusion (Birkholzer et al., 2009; Oldenburg et al., 2011; Keating et al., 2012). Oldenburg et al. (2011) concluded that if overpressurization is moderate and salinity is high, upward brine migration will be limited and a new steady state can be achieved with the fresh water/saline water boundary well below the bottom of the aquifer. However, if overpressurization is high or salinity is low, brine will migrate into the shallow aquifer. Keating et al. (2012) used simulations and contrasting observations at two natural analog sites to conclude that the geometry of the leaky pathway will affect the likelihood of brine intrusion. They concluded that narrow features (wellbores, narrow fault zones) are more likely to convey brine into the shallow aquifer than broad leaky features. Birkholzer et al. (2009) analyzed an idealized multi-layer aquifer/aquitar system without a vertical conduit and concluded that brine intrusion would be unlikely in such a setting.

The impact of brine and CO₂ intrusion on water quality in the shallow aquifer has been the focus of many recent studies. Laboratory experiments where sediments are exposed to CO₂ have established the potential for trace metal release (Little and Jackson, 2010; Smyth et al., 2009). Likewise, controlled field experiments have established that CO₂ release can cause increases in trace metal concentrations (Kharaka et al., 2010; Trautz et al., 2013; Peter et al., 2012). In most cases, the increase in trace metal concentrations was very subtle and concentrations did not approach or exceed drinking water standards. Some laboratory experiments (Carey et al., 2009) and natural analog studies (Keating et al., 2013) suggest that trace metal elevation will be temporary. As buffering reactions proceed, trace metals can precipitate or re-adsorb (Aiuippa et al., 2005). Apart from trace metals, saline brines can be a significant threat to ground-water and NaCl will not be subject to significant buffering. It is likely that each site will have a unique geochemical response to CO₂ leakage.

2. Site description

The Springerville–St. Johns dome is a shallow (200–700 m) natural CO₂ reservoir near the southern edge of the Colorado Plateau (Moore et al., 2005), reported to contain as much as 445 billion m³ of CO₂ (Stevens et al., 2005). The CO₂ is closely associated with a relatively young volcanic field (<3 Ma) (Moore et al., 2005). The reservoir is hosted in an alternating sequence of discontinuous sandstone, limestone, shale, and anhydrite layers of the Permian Supai Group. Below the Supai is fractured Precambrian granite basement; above are the Glorieta Sandstone and San Andres Limestone, which are regionally extensive aquifers. These, in turn, are capped by confining layers (shales of the Moenkopi and Chinle Formations). Northwest trending faults and related folds also cross the dome, with the Coyote Wash fault bounding the western margin of the dome.

The Tucson Electric Power (TEP) company wells produce groundwater from the Glorieta Sandstone (equivalent to the Coconino Sandstone). Regionally, this sandstone unit is the most productive unit of the C aquifer, the predominant groundwater source in the Colorado Plateau/Little Colorado River basin of Arizona and western New Mexico (Hoffmann et al., 2006). The production wells are located in the Coyote Wash fault zone (see Fig. 1). The wells have high levels of dissolved CO₂, which has been problematic for TEP, requiring that most of their groundwater production wells be replaced with stainless-steel well strings due to

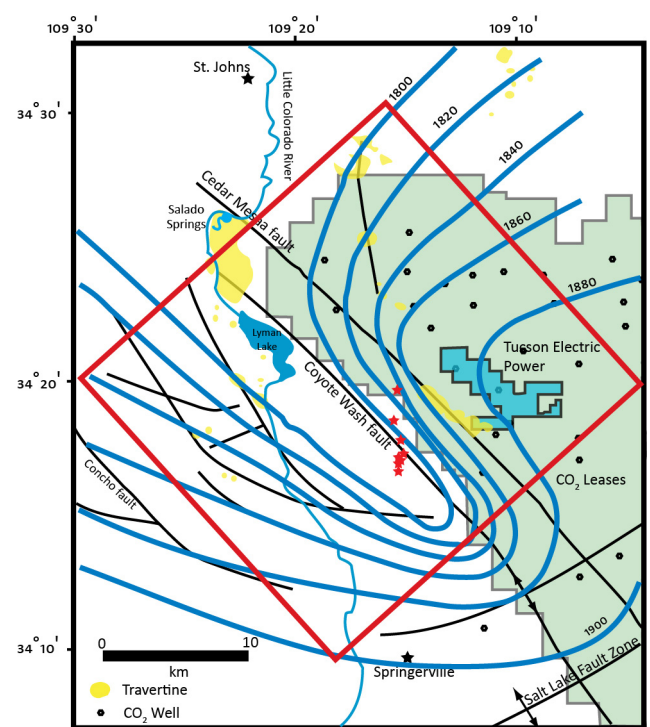


Fig. 1. Site map of study area at Springerville–St. John. Water levels are indicated by blue contours. Red dots show wells sampled. Red box illustrates extent of numerical model. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

corrosion problems (TEP personal communication). Previous workers have concluded that the elevated dissolved CO₂ observed in the TEP groundwater wells and at Salado Springs is sourced from the underlying CO₂ dome, and that this CO₂ is migrating upwards primarily along the Coyote Wash Fault zone (Gilfillan et al., 2011; Moore et al., 2005). Furthermore, the extensive travertine deposits in the area are attributed to CO₂–rock–water interaction moving carbonate-saturated groundwater to the surface along faults (Crumpler et al., 1994). The noble gas and stable isotope geochemistry of the CO₂ source and dissolved gases in the groundwater suggests a mantle-derived magmatic source for the CO₂ that is likely associated with the Springerville volcanic field (Gilfillan et al., 2008, 2011).

Allis et al. (2005) conducted multi-phase reactive-transport simulations of the reservoir, leakage along the fault zone, and travertine deposition. They were able to explain the timing and total volume of travertine deposition by assuming an influx of CO₂ into the base of the fault (from below) of ~63 kTon/year CO₂. Their simulations showed a transient overpressurization of the reservoir, leading to a rise in the water table elevation and broad area of water and CO₂ discharge.

Less is known about the migration of brine from the reservoir layers into the shallow aquifer. The highest measured salinity in the aquifer (2150 ppm, Moore et al., 2005) is elevated compared to regional groundwater but much less saline than deeper water (at least 4210 ppm and probably much higher due to anhydrite layers). Compared to the C aquifer chemistry at locations distal to the Springerville–St. Johns CO₂ system, the salinity observed here is significantly higher. For example, 200 km northwest of Springerville, the C aquifer has a chloride levels <115 mg/l, with arsenic levels below the maximum contaminant level as defined by the U.S. EPA (Hoffmann et al., 2006). It is unclear whether the slightly elevated salinity is related to the rising CO₂ from depth. Simulations developed by Keating et al. (2010) suggested that upward flow

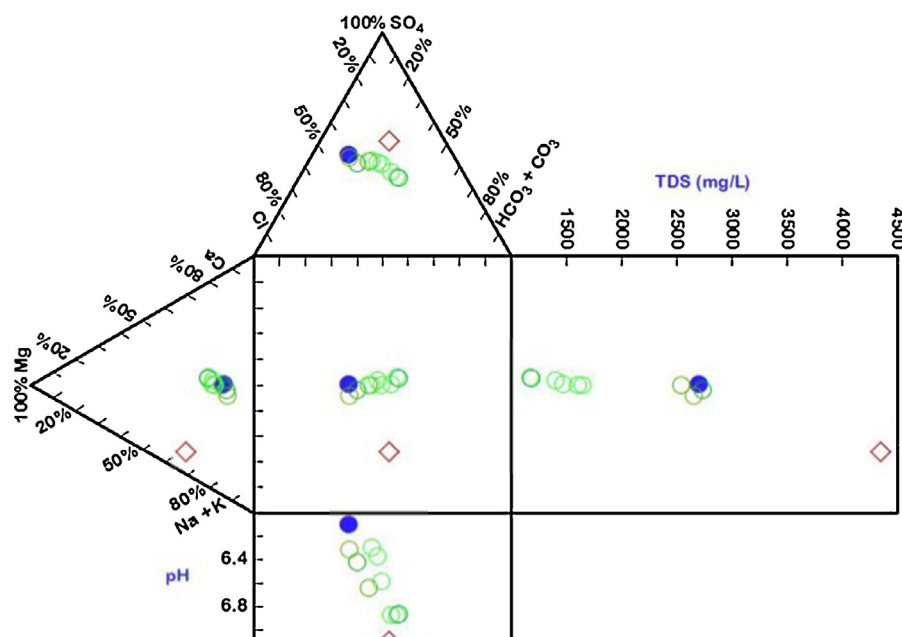


Fig. 2. Durov diagram showing variation in major ion chemistry, pH, and TDS. Blue circle is Salado Springs, open green circles are production wells, red diamond is a reservoir sample (Moore et al., 2005). (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

of free-phase CO₂ from depth along the Coyote Wash fault zone could not displace the fresh water/saline water boundary upwards more than ~100 m. It is interesting that according to water quality records maintained by Montgomery and Associates (2011), there has been little to no increase in salinity in the TEP production wells over time, despite relatively large amounts of extraction.

There are several conclusions to be drawn from the observations in and above the Springerville–St. Johns reservoir. One, although the integrity of the caprock is sufficient to preserve a significant reservoir of CO₂ (and high helium, ~1%, Rauzi, 2003) within the deeper sedimentary units, high levels of deep-source dissolved CO₂ in the shallow aquifer demonstrate a pathway for CO₂ migration. A likely pathway to explain the CO₂ occurrence in shallow water is the nearby relatively broad, high-permeability fault zone (Coyote Wash Fault zone). These characteristics have combined to make the Springerville–St. Johns CO₂ dome a natural analog for leakage from a geologic carbon sequestration storage site. A variety of questions can be asked including (1) can the CO₂ be identified in the shallow groundwater; (2) can CO₂ migration along the fault zone explain the levels of dissolved CO₂ seen in the aquifer; (3) is the CO₂ migrating alone or with brine; and (4) has the leakage from the CO₂ storage site affected the shallow groundwater chemistry?

3. Water chemistry

3.1. Methods

Groundwater samples were collected from 8 wells that Tucson Electric Power uses to produce cooling water for the Springerville Generating Station (Fig. 1). These 8 wells were in service at the time of sampling. Two travertine spring mounds and one shallow alluvial well were also sampled at Salado Springs (Fig. 1). The production wells operate at high flow rates so purging of the well bore was unnecessary, and these wells are closed systems at the well-head location preventing degassing and oxygenation during pumping to the surface. These wells are also constructed of stainless steel to minimize corrosion from CO₂-charged groundwater. Water was collected from taps located either on the wellhead or on piping leading directly from the wellhead. Prior to sample collection, water

was allowed to flow slowly (to minimize degassing) until temperature, pH and conductivity stabilized, usually within a few minutes. At Salado Springs, grab samples were collected from the two spring mounds. The alluvial well was under slight artesian pressure so it produced water from a spigot that was allowed to discharge until field parameters stabilized. Samples for major cation and trace metals analyses were field filtered (0.45 μm) and acidified with trace metal grade nitric acid. Samples for anions, alkalinity and stable isotope analyses were collected unfiltered with no headspace. Carbon stable isotope samples were collected into gas tight bottles to prevent degassing and fractionation prior to analysis.

All samples were processed and analyzed at the Los Alamos National Laboratory Earth and Environmental Sciences Geochemistry and Geomaterials Research Laboratories (GGRL). Major cations and trace metals were measured by ICP-OES and ICP-MS, and anions were determined by Ion Chromatography. Stable isotope ratios of dissolved inorganic carbon, and oxygen and hydrogen in water were determined by continuous flow isotope ratio mass spectrometry (CF-IRMS) on a GV Instruments Isoprime mass spectrometer attached to a Multiflow peripheral instrument. Results are reported using standard delta notation in per mil (‰). δ¹³C is reported versus PDB, and δ¹⁸O and δD are reported versus SMOW. Standard deviations on δ¹³C, δ¹⁸O and δD measurements based on in-house and international standards were 0.13, 0.12 and 0.5‰ respectively.

4. Results

Table 1 summarizes the temperature, field pH and major ion element chemistry for the well and spring samples. For the purpose of this study, we consider major elements to be Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl[−], and the anion complexes: HCO₃[−], SO₄^{2−}. The log pCO₂ and saturation indices for calcite and dolomite were determined using PHREEQC (Parkhurst and Appelo, 1999) using the Wateq4 database. Calcite was near saturation (|log SI| < 0.5) in 5 samples, undersaturated in six. Dolomite was supersaturated (log SI > 0) in about half of the samples. All other mineral phases were undersaturated in the samples and are not reported. Selected minor and trace elements are reported in Table 2. Only elements that were detected or are

Table 1

Field parameters and major element chemistry (mg/l) for TEP wells and Salado Springs.

Sample ID	T (°C)	pH	Ca	Cl	HCO ₃ ⁻	K	Mg	Na	SO ₄	Charge balance (%)	Log pCO ₂ ^a	Log SI ^a	
												cal	dol
P-7a	16.6	6.9	135	146	458	10	39	131	259	-3.7	-1.4	-0.1	0.5
P-8a	25.3	6.3	165	190	522	17	45	182	345	-2.1	-0.9	-0.6	-0.4
P-9a	25.3	6.4	315	491	754	27	54	382	710	-1.1	-0.8	-0.1	0.3
P-10a	24.8	6.3	184	213	563	17	45	205	379	-1.9	-0.9	-0.6	-0.4
P-16	22.7	6.9	139	138	467	12	41	137	252	-0.6	-1.4	-0.0	0.8
P-18	22.4	6.7	301	414	710	26	58	338	692	-3.5	-1.0	0.1	0.8
P-19	24.0	6.6	188	215	559	20	50	211	402	-1.0	-1.1	-0.2	0.4
P-20	24.9	6.4	163	175	516	16	42	166	323	-2.4	-1.0	-0.6	-0.3
Salado 1 (spring)	17.1	6.1	322	473	744	25	61	359	710	-3.8	-0.7	-0.8	-0.9
Salado 2 (spring)	17.3	6.2	309	449	758	26	59	380	707	-3.0	-0.8	-0.6	-0.6
Salado 3 (Well)	14.8	6.2	307	449	769	27	60	387	688	-1.2	-0.8	-0.7	-0.7

^a Log pCO₂ and log saturation index (SI) calculated using PHREEQC (Parkhurst and Appelo, 1999). cal = calcite; dol = dolomite.**Table 2**

Selected minor and trace element chemistry (mg/l) for TEP wells and Salado Springs.

Sample ID	As	B	Ba	Br	Cs	F	Fe	Li	Mn	Rb	SiO ₂	Sr	U
P-7a	0.003	0.30	0.023	nd	0.02	1.8	nd	0.18	0.01	0.044	15	1	nd
P-8a	0.012	0.53	0.022	nd	0.02	2.3	0.3	0.24	0.01	0.055	16	2	nd
P-9a	0.042	0.77	0.019	nd	0.04	1.9	0.8	0.57	0.04	0.107	16	3	nd
P-10a	0.018	0.46	0.023	nd	0.02	1.9	0.2	0.26	0.02	0.062	17	2	nd
P-16	0.011	0.35	0.025	nd	0.02	1.9	0.3	0.18	0.01	0.049	15	1	nd
P-18	0.035	0.71	0.016	0.1	0.03	2.6	0.8	0.47	0.03	0.100	15	3	nd
P-19	0.016	0.79	0.022	0.2	0.02	1.8	0.4	0.25	0.02	0.069	16	2	nd
P-20	0.014	0.41	0.024	nd	0.02	2.2	0.2	0.23	0.02	0.061	15	1	nd
Salado 1 (spring)	0.016	0.75	0.017	0.2	0.03	2.3	nd	0.55	0.03	0.100	17	3	nd
Salado 2 (spring)	0.009	0.88	0.015	0.2	0.03	2.2	nd	0.50	0.02	0.098	17	3	nd
Salado 3 (Well)	0.021	0.81	0.015	0.3	0.03	2.1	15	0.53	0.15	0.102	18	3	nd

of particular interest for groundwater quality (e.g., uranium) are tabulated.

A Durov diagram, Fig. 2, shows the variation in water chemistry at the site. For comparison, we included a sample from the deep reservoir collected by Moore et al. (2005). This figure illustrates the geochemical distinction between the shallow aquifer and the deep reservoir. The deep reservoir is enriched with respect to sodium, has a higher pH and TDS. Scatterplots show a consistent relationship between all major elements in the shallow aquifer. Fig. 3 presents representative relationships between HCO₃⁻, Cl⁻ and SO₄²⁻. The pattern that emerges is a linear array with a high concentration end-member that includes wells P-9a and P-18 and all the Salado Spring locations. The other wells create a lower concentration linear array. There is a gap between the high concentration end member and lower concentration array that is ~200 mg/l in terms of chloride. These patterns also hold for Li and Rb, as shown by the strong correlation with chloride (Fig. 4). Arsenic, the only trace element that was found elevated above EPA MCLs (10 ppb, or 0.010 mg/l), shows a slightly different behavior. The linear array exists for the P-well samples, but note that the Salado Spring samples fall consistently off this trend (Fig. 2, As vs. Cl) where arsenic concentrations are significantly lower than P-9a and P-18.

Results of the stable isotope analyses are reported in Table 3. Stable isotopes O and H are consistent with regional meteoric water values (Bills et al., 1990; Kendall and Coplen, 2001). The $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) measured in this study range from -1.6 to 0.28‰ (PDB). Gilfillan et al. (2011) found similar values in these wells, but also were able to access P-14 that returned a value of 0.9‰. The $\delta^{13}\text{C}_{\text{DIC}}$ from deep CO₂ wells in the gas resource to the east of the production well field fall in a narrow range between -3.8 and -3.6‰ (PDB) (Gilfillan et al., 2008, 2009). Although previous workers did not see a strong signal in the carbon isotopes, we see a correlation between P-well $\delta^{13}\text{C}_{\text{DIC}}$ and the major and trace element chemistry. Essentially, the highest carbon isotopes values (Table 3; P-9a, P-18 and P-14) correlate with the high concentration

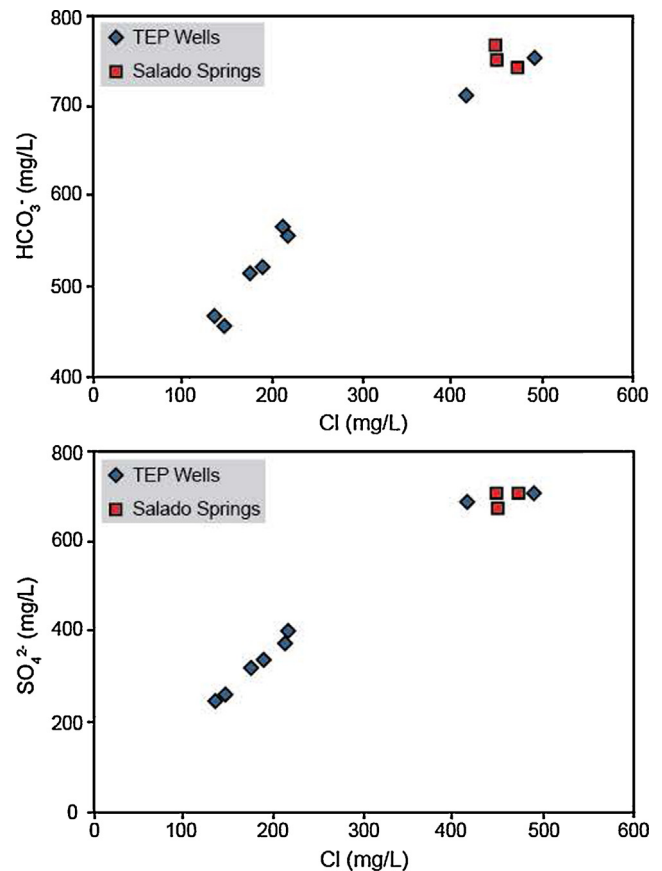


Fig. 3. Selected trace elements (As, B, Li and Rb) versus chloride content. The binary mixing trend seen in the major elements is preserved in the trace elements. Note that the As concentrations at Salado Springs fall off this trend, with lower concentrations than predicted by the mixing line.

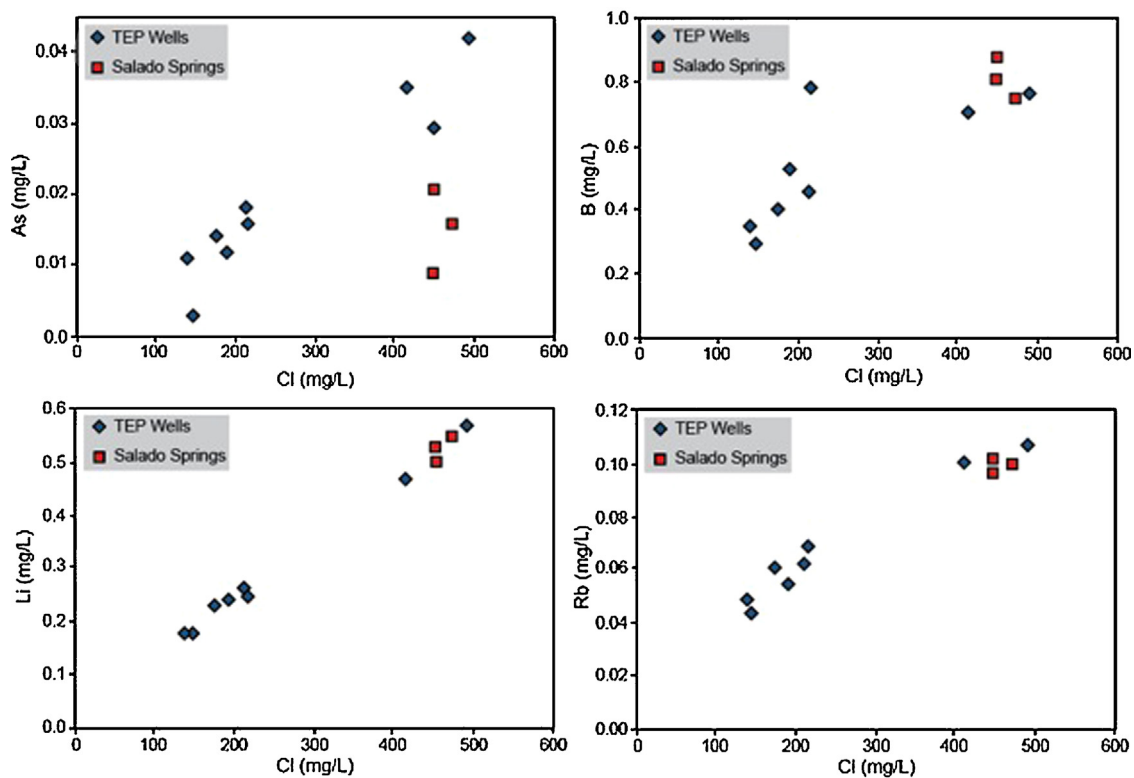


Fig. 4. Selected trace elements (As, B, Li and Rb) versus chloride content. The binary mixing trend seen in the major elements is preserved in the trace elements. Note that the As concentrations at Salado Springs fall off this trend, with lower concentrations than predicted by the mixing line.

(more saline) end-member. Similar to arsenic, the Salado Springs samples fall off this trend with a lower $\delta^{13}\text{C}_{\text{DIC}}$.

5. Discussion

The major ion and trace element trends observed in the groundwater and Salado Springs can be explained by simple mixing of two sources (Figs. 3 and 4). It appears that a CO_2 -rich end member with higher salinity and elevated trace element concentrations is mixing with more dilute groundwater in the aquifer. This is supported by the co-variation of chloride with bicarbonate, sulfate, and most other major and trace elements.

However, a simple mix of two end-members is not adequate to explain the carbon isotope trends observed. As Gilfillan et al. (2011) noted, the carbon isotopic composition of the groundwater is difficult to explain based on measurements of the deep CO_2 source; whereas, gas migration and dissolution could explain the

noble gas compositional trends. Fig. 5 shows that the $\delta^{13}\text{C}_{\text{DIC}}$ and bicarbonate content of the proposed deep CO_2 source do not fall on the mixing trend observed in the overlying aquifer. Also, the Salado Spring samples seem to fall off this trend. A proposed mechanism to

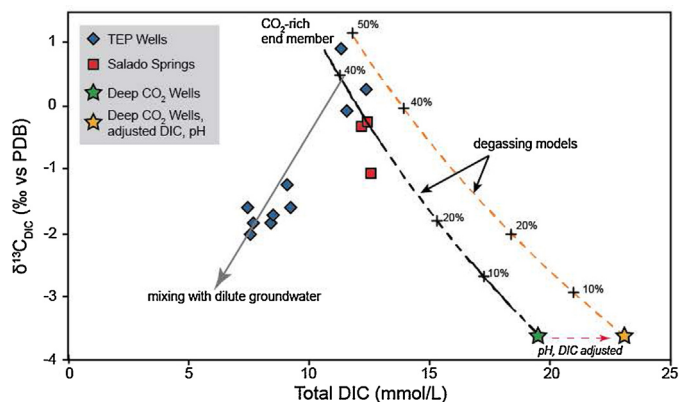


Fig. 5. Carbon stable isotope composition of the dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) versus total dissolved inorganic carbon (DIC) – for the TEP wells, Salado Springs, and the deep CO_2 wells (Gilfillan et al., 2011). The TEP wells form an apparent binary mixture between high $\delta^{13}\text{C}_{\text{DIC}}$ and high DIC- end-member and low $\delta^{13}\text{C}_{\text{DIC}}$, more dilute groundwater. Salado Springs fall off this trend. A Rayleigh degassing models for groundwater at 30 °C can explain evolution of the deep CO_2 source to the high concentration end-member seen in the groundwater (modified from Newell et al., 2008; Gilfillan et al., 2009). The carbon isotope fractionation between the degassing CO_2 and the total DIC pool for the model is calculated based on the speciation of DIC ($\text{CO}_2(\text{aq}) + \text{HCO}_3^-$) using the approach of Deines et al. (1974) and Gilfillan et al. (2009): $\varepsilon^{13}\text{C}_{\text{DIC}-\text{CO}_2(\text{g})} = x(\varepsilon^{13}\text{C}_{\text{H}_2\text{CO}_3(\text{aq})-\text{CO}_2(\text{g})}) + (1-x)(\varepsilon^{13}\text{C}_{\text{HCO}_3^-(\text{aq})-\text{CO}_2(\text{g})})$, where x is the fraction of H_2CO_3 and $(1-x)$ is the fraction of HCO_3^- . The speciation is calculated using PHREEQC (Parkhurst and Appelo, 1999) and the reported water chemistry for deep CO_2 well 11–21 (Moore et al., 2005). Since degassing during sampling may have impacted the pH for this well, we adjusted the pH and total DIC by adding CO_2 to reach calcite saturation (using PHREEQC), and present a second degassing model based on this starting chemistry.

Table 3
Stable isotopes of O, H and C for TEP wells, Salado Springs, and deep gas wells.

Sample ID	$\delta^{18}\text{O}$ ‰ (SMOW)	δD ‰ (SMOW)	$\delta^{13}\text{C}_{\text{DIC}}$ ‰ (PDB)
P-7a	−10.96	−79.55	−1.62
P-8a	−10.65	−78.17	−1.78
P-9a	−10.76	−78.03	0.28
P-10a	−10.89	−78.27	−1.63
P-16	−10.81	−78.91	−1.87
P-18	−10.92	−79.10	−0.08
P-19	−10.91	−78.11	−1.29
P-20	−10.63	−75.88	−1.87
Salado 1 (spring)	−10.59	−78.57	−0.33
Salado 2 (spring)	−10.72	−78.80	−0.25
Salado 3 (Well)	−10.78	−79.41	−1.09
P-14 ^a	nr	nr	0.90
Deep CO_2 wells ^a	nr	nr	−3.6 to −3.8

^a From Gilfillan et al. (2011).

explain the data is open system Rayleigh degassing (Fig. 5) (modified from Newell et al., 2008; Gilfillan et al., 2009). The fractionation between the DIC pool in the groundwater and the degassing CO_2 is calculated assuming a temperature of 30°C and considering the speciation of the DIC pool (aqueous CO_2 and bicarbonate) (Deines et al., 1974; Gilfillan et al., 2009). The starting DIC and chemistry for speciation calculations using PHREEQC are based on State Well 11–21 reported in Moore et al. (2005). Although the charge balance for this water chemistry is acceptable, the reported pH may be altered from in situ conditions due to degassing during sampling. Since the speciation is sensitive to the pH, we also present a second degassing model using modified starting water chemistry (Fig. 5). The DIC content and speciation and pH of the groundwater are modified in PHREEQC by adding CO_2 until calcite saturation is reached (SI adjusted from 0.4 to 0.0). These simple models show that 40–50% degassing can evolve the CO_2 reservoir source fluid to the $\delta^{13}\text{C}_{\text{DIC}}$ and total DIC concentration observed for the high concentration end-member. This model is path independent in that this degassing could occur during fluid ascent from source to groundwater, or from the shallow groundwater after ascent and mixing. This model may also explain the two Salado Spring samples collected at travertine spring mounds, with a slightly smaller degree of degassing. The outlier Salado Spring sample is the shallow alluvial well sample; this sample could be experiencing mixing with alluvial groundwater. Alternatively, microbial activity at Salado Springs could be modifying the carbon isotopic composition through processes such as dissolved organic matter oxidation or microbially mediated calcite precipitation. However, given the large inorganic carbon pool in the spring waters, these processes would not significantly alter the dissolved inorganic carbon concentration. It is important to note that this Rayleigh degassing model cannot be modified to explain the dilute end-member of the groundwater trend. We suggest that a CO_2 -rich fluid is migrating and evolving due to degassing and that this evolved fluid then mixes with groundwater to create the binary trend. The primary importance of dissolved CO_2 transport rather than free-phase transport is significant.

Also of interest is the source of salinity and trace elements creating the observed mixing trends. The values of chloride and arsenic (491 and 0.042 mg/l) are higher than background values ($<2\ \mu\text{g/l}$) observed in waters to the north (Hoffmann et al., 2006). Emplacement of the Springerville volcanic field could have introduced trace elements such as As, Li and B due to magmatic devolatilization and local hydrothermal circulation (Condit et al., 1989; Guilbert and Park, 1986). However, this cannot explain the addition of significant amounts of chloride, sulfate and other major elements (e.g., calcium, sodium). A more plausible source of brine and trace metals is the Supai Group encountered along flow paths below the aquifer. High arsenic values up to 1000 ppb in Verde Valley springs southwest of Springerville, are attributed to sources within the Supai Group (Foust et al., 2004; Johnson et al., 2012). Evaporite horizons, including thick anhydrite beds in the Big A Butte Member show evidence of CO_2 -brine-rock interaction (e.g., formation of secondary dawsonite) (Moore et al., 2005) are potential sources of these trace elements in the Supai Group. Modern salts are known to concentrate trace elements such as As, B, and Li and result in associated groundwater enrichment in these elements (Concha et al., 2010; Risacher and Fritz, 1991).

A notable exception to the binary mixing trends is the concentration of arsenic at Salado Springs (Fig. 4). Based on other major and trace elements, Salado Springs appears quite similar to wells P-9a and P-18 that define the high concentration end member. It is beyond the scope to fully investigate what processes are responsible for lowering the arsenic concentration, while not impacting other trace elements. However, microbial processes coupled to iron and sulfur redox chemistry in the springs could be responsible for

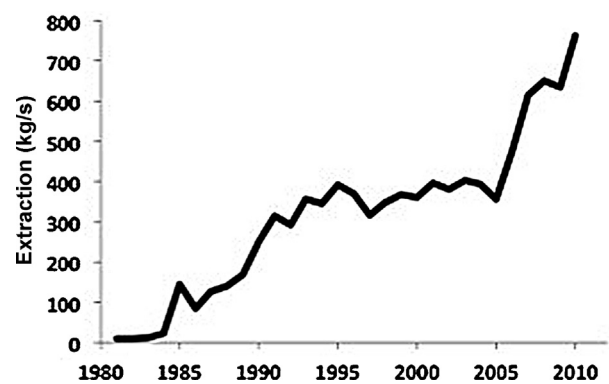


Fig. 6. Rate of extraction for TEP production wells from 1981 to 2010 (total for all wells).

lowering arsenic concentration through the precipitation of iron oxides (Kirk et al., 2004). This interpretation is also consistent with the $\delta^{13}\text{C}_{\text{DIC}}$ of the springs falling off the trend. The carbon stable isotopic values could have been lowered by microbial processes that preferentially use the lighter carbon isotope (Sharp, 2006).

In summary, evidence from the water chemistry measurements is consistent with a conceptual model of brackish or saline water and CO_2 moving up along the fault zone. The water transports salinity and trace metals from the layers within the Supai Group. Mixing with shallow dilute groundwater reduces concentrations; the resulting variability can be explained by a conservative, non-reactive mixing. Waters sampled in and near Salado Springs show evidence of some reactions, perhaps biogeochemical. Stable isotopes suggest the CO_2 has undergone significant degassing. This suggests the CO_2 moved upward in the dissolved phase, and degassed as pressures decrease or as the water mixed with shallow groundwater. The common theme of upward flow of CO_2 -enriched water explains the transport of CO_2 , major and trace elements in this system. This does not preclude the possibility that CO_2 -induced changes in shallow water quality might be occurring here, rather, such changes are probably much more subtle than the changes caused by mixing with saline water.

6. Fault permeability

We used hydrologic data and groundwater flow simulations to explore the hydrologic characteristics of the fault system. This system is unique in that production wells are completed near the fault, and complete extraction and drawdown data are available for the wellfield. A substantial amount of water has been produced from these wells (see Fig. 6) with relatively minor drawdown (34 m at most; see Fig. 1). An interesting feature of the drawdown response is that monitoring wells on the upthrown side of the fault (to the north) have experienced **no** measurable drawdown (see Fig. 1). We developed a series of 3-D groundwater flow simulations with the goal of developing and testing hypotheses about the hydrologic characteristics of the fault zones, and attempting to match the drawdown data (to first order). There is considerable uncertainty about the properties of the rock layers and the fault zone; to our knowledge there are no site-specific hydraulic testing results available. Therefore, for each conceptual model of the fault system, we consider the hydrologic properties of the rocks to be uncertain parameters that can be optimized to best match measured drawdowns. If two conceptual models match the drawdowns equally well, they are equally likely.

We assume the same hydrostratigraphy for all the models, since this is fairly well known (Fig. 7). A simplified hydrostratigraphic

Table 4
Sum of squared errors for simulated drawdowns, using three conceptual models of the fault zone.

Well types	Flow-neutral fault zone	Distinct fault zone, shallow only	Distinct fault zone, full penetration
Production wellfield ($n = 15$)	1087	5358	598
Monitoring wells ($n = 6$)	133	10	6

model accounting for the Precambrian basement, four units of the Supai formation, the Glorieta Sandstone, and the San Andreas Limestone was developed based on interpretations in Moore et al. (2005) and Rauzi (1999). This 3-D model reproduces the measured offset in all the rock layers along the Coyote Wash fault. All layers above the San Andreas, including the Chinle Formation, were combined into a single undifferentiated unit.

Boundary conditions and annual extraction rates were defined in the same way for all models. The lateral model extent ($20 \text{ km} \times 20 \text{ km}$) was selected to be large enough to encompass all the wells with transient head data available yet not so large as to be computationally intractable. Unfortunately none of the lateral boundaries coincide with groundwater divides. The closest groundwater divide, according to the Arizona Water Atlas (2011), is much too distant to the south to be a practical model boundary for this study. To account for the natural inflow and outflow of shallow groundwater along model boundaries (true flux rates are unknown), constant pressure boundary conditions were assigned along all four boundaries in the shallow (above Supai) layers. Pressures were defined in accordance with regional water level data derived from the Arizona Department of Water Resources database (2011). The upper model boundary was considered to be no-flow, due to the confining nature of the Chinle formation. Transient simulations were conducted, applying annual extraction rates to each of 14 TEP production wells over a 30-year period (see Fig. 6). Initial pressures were specified to be hydrostatic. At the end of each transient simulation, total drawdown over the entire period was compared to measured drawdown at each well with available data (21 wells total). Simulations were single-phase (water only), executed using the code FEHM (Zyvoloski, 1997) developed at Los Alamos National Laboratory.

We tested three conceptual models for the fault zone: a 'flow neutral' model, and two hydrologically distinct fault zones: one, penetrating only to the base of the deepest production well ($\sim 1525 \text{ m}$), the other, penetrating the entire thickness of the model. In each case, PEST was given the freedom to vary permeabilities and

Table 5
Rock properties and sensitivities specific storage $10^{-4.0}/\text{m}$ intrinsic permeability ($\log 10 \text{ m}^2$).

	Unit	Permeability	Sensitivity
Supai formation	Basement	−17.	–
	Amos Wash	−14.	–
	Big Butte	−14.4	–
	Ft. Apache	−12.1	–
	Corduroy	−14.7	9.077109E−03
	Glorieta Sandstone ^a	−16.	1.769560E−02
	San Andreas Limestone	−11.9	0.850563
	Upper units	−11.0	0.793787
	Fault zone (upper, $z > 1525 \text{ m}$)	−11.3	4.91668
	Fault zone (lower, $z < 1525 \text{ m}$)	−12.5	8.54851

^a Note: Due to the very low sensitivity of this parameter, the 'estimated' value (−16.) is not meaningful.

specific storage of all rock layers and (if present) fault zones within a wide range (10^{-11} – 10^{-16} m^2 and 10^{-2} – $10^{-6}/\text{m}$, respectively).

Results are summarized in Tables 4 and 5. Of the three conceptualizations of the fault zone, the model that considered the fault zone distinct, deep, and permeable outperformed the other two conceptualizations. The 'flow neutral' fault zone conceptual model tended to overpredict drawdowns in the monitoring wells on the upthrown side of the fault (Table 3). Parameter sensitivities (Table 5) show that the highest sensitivity is to the permeabilities of the fault zone, particularly the deep portion. Because of the high sensitivities, these permeability estimates are associated with a higher level confidence. Collectively, these results suggest that to reproduce measured drawdowns in both the wellfield and the monitoring network to the northeast requires a hydrologically distinct fault zone that extends much deeper than the wellfield itself. The match is not perfect (see Fig. 8), as is to be expected

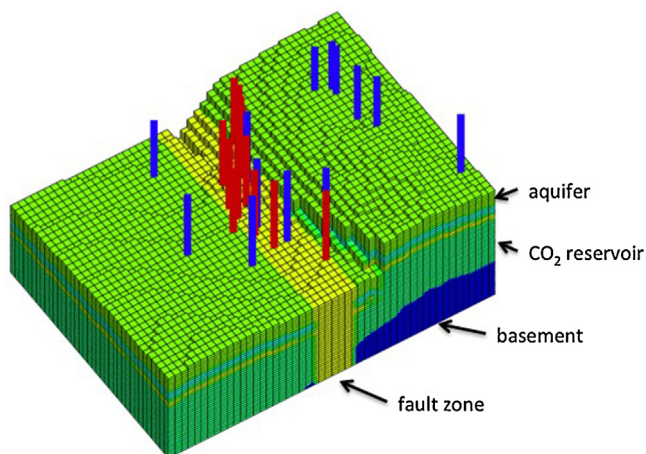


Fig. 7. Three-dimensional grid for the production simulations. Blue lines show location of monitoring wells; red lines show location of production wells. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

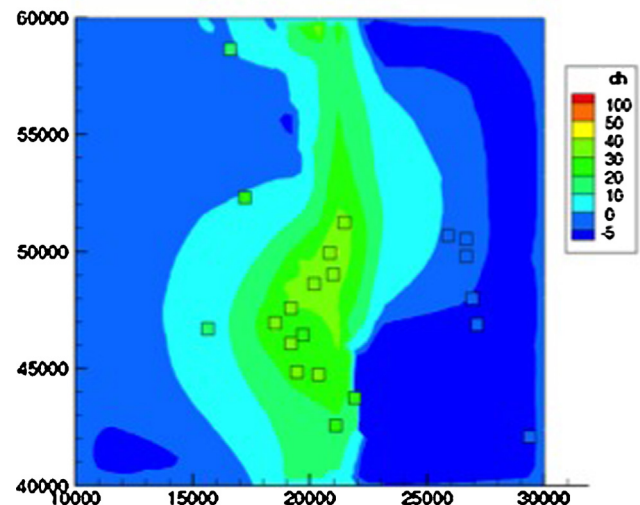


Fig. 8. Water level drawdown over 29 years in uppermost model layer (m). Contours show simulation results, filled squares indicate measurements.

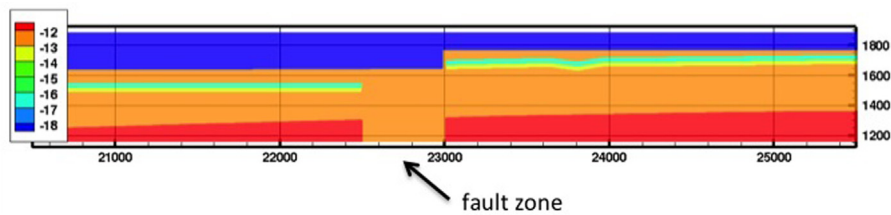


Fig. 9. 2-D Simulations of buoyancy-driven CO₂ migration in the presence of a permeable fault zone: permeability variation.

when the hydrostratigraphy is generalized; however the simulated drawdowns are similar to those measured.

By examining inflows along the constant pressure boundaries we were able to confirm that the water extraction does increase inflow along the closest (southwestern) model boundary. However, the increase in inflow is only about 15% of the extraction; the remaining 85% is derived from storage. Because of this relatively small effect, we do not believe these results are particularly sensitive to the pressure boundary conditions.

This analysis demonstrates that the high permeability fault feature that allowed significant upflow of CO₂ in the past, leading to large travertine deposits, is still a modern hydrologic pathway. The production wells are extracting water that comes, to some extent, from depth. Unlike previous studies, this analysis constrains the depth and permeability of the fault zone.

7. The unlikely co-existence of a gas reservoir and a broad, leaky conduit

There are multiple lines of evidence, including new analyses presented here, that the St. Johns–Springerville CO₂ reservoir is penetrated by a broad, highly permeable fault zone. How, then, can an estimated 445 billion m³ of buoyant CO₂ gas remain at depth? This question is directly relevant to engineered CO₂ sequestration. Here we present multi-phase (CO₂/water) flow simulations to

investigate the stability of a shallow gas reservoir in the presence of a wide leaky fault.

To simplify the system we extracted a 2-D cross-section from the 3-D model described above. The cross-section is 100 m thick, and represents approximately 1/500th the total reservoir volume (see Fig. 9). We initialized the simulations with a gas-phase CO₂ reservoir in multiple layers, according to the conceptual and numerical models presented by Allis et al. (2005). The pore space in the gas reservoir is 60% free-phase CO₂, 40% water. The gas is allowed to dissolve in the water up to the pressure/temperature-dependent solubility limit. The total CO₂ mass of the initial reservoir is $\sim 7 \times 10^8$ kg, approximately 30% in the dissolved phase. Pressure is initially hydrostatic, with a slight horizontal gradient in the shallow aquifer (.028). This gradient is within the range of measured gradients in the shallow aquifer at Springerville (approximately 0–0.03; Fig. 1).

Figs. 10 and 11 illustrates the rapid changes that occur in the first 300 days of simulation. Due to buoyancy, the gas begins to move upward along the broad high-permeability fault zone. Quickly, the fault zone is filled with a dissolved CO₂ plume, which eventually moves away from the fault in the shallow aquifer. After a short time, however, the rate of gas depletion of the reservoir sharply declines.

The rate of gas depletion, shown in Fig. 12, becomes approximately a constant value of 6×10^5 kg/year. To place this in context

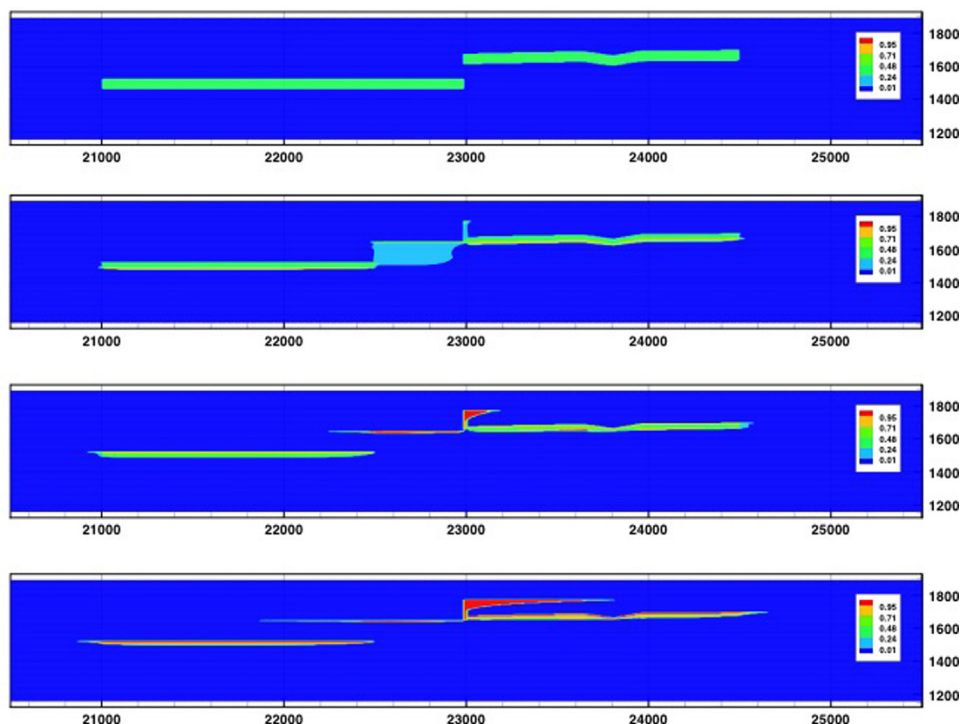


Fig. 10. 2-D Simulations of buoyancy-driven CO₂ migration in the presence of a permeable fault zone. (a) 0 days, (b) 8 days, (c) 98 days, and (d) 300 days.

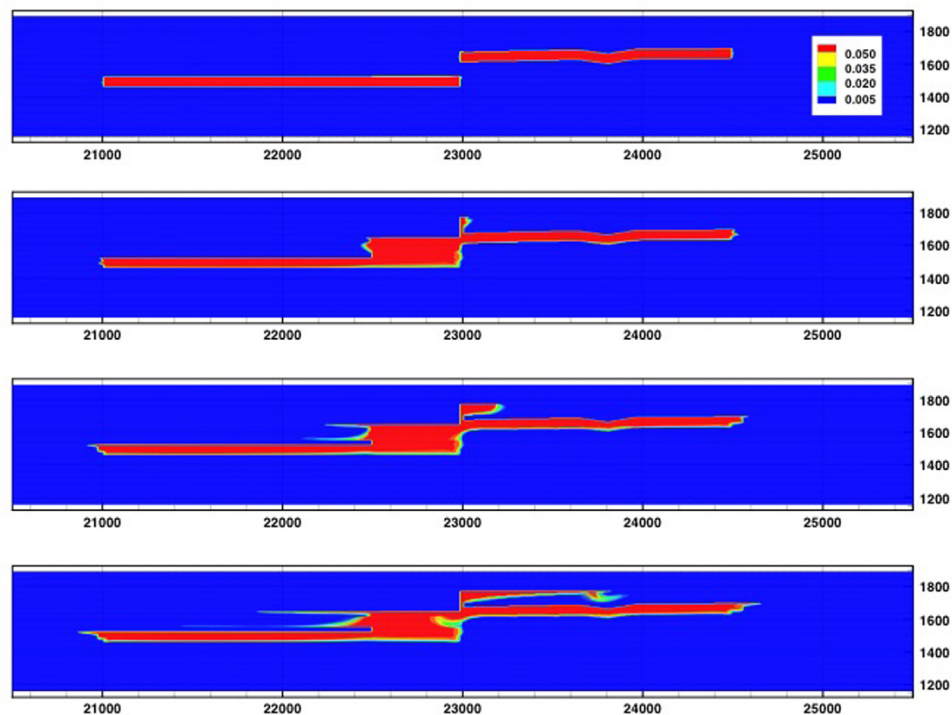


Fig. 11. 2-D Simulations of buoyancy-driven CO₂ migration in the presence of a permeable fault zone. Dissolved CO₂ mass fraction (a) 0 days, (b) 8 days, (c) 98 days, and (d) 300 days.

of the reservoir at Springerville, this is significantly smaller than the leakage rate inferred by Allis et al. (2005) during the period of high CO₂ degassing and travertine deposition. Our finding is thus consistent with the view that contemporary degassing of the Springerville reservoir is much less than during an earlier period in its history when travertines were being formed (Moore et al., 2005).

Stevens et al. (2005) report CO₂ in place at Springerville as 16Tcf (trillion cubic feet at 21 °C and atmospheric pressure) or 445 billion m³. At representative in situ conditions ($T=25^{\circ}\text{C}$, $P=4.5\text{ MPa}$), CO₂ density is approximately 60 times higher (112 kg m^{-3} vs. atmospheric 1.8 kg m^{-3}) and the volume of gas in place is therefore ~ 7.4 billion m³. The mass of CO₂ is reported at 830 Mt. If the leak rate indicated by the 100-m thick cross-sectional model is scaled to a 50 km along-strike length ($6 \times 10^5 \times 500 = 3 \times 10^8\text{ kg/year}$) then it is possible to address the following question: could a natural gas reservoir sustain these rates of depletion for long periods of time? If there were no CO₂ replenishment at depth from the mantle, it would take approximately

2800 years to deplete a reservoir the size of St. John's Dome at Springerville.

An interesting aspect of these results is that a large plume of dissolved CO₂ is maintained within the fault zone long after the primary upward pulse of buoyancy-driven gas phase. The geometry of this plume is consistent with the presence of high levels of dissolved CO₂ in the TEP wells. The slow leak rate of CO₂ gas (Fig. 12) is probably adequate to maintain this dissolved CO₂ plume indefinitely.

Although we used some of the features of the Springerville site, such as the hydrostratigraphy and fault geometry, to inform the simulations, these simulations are not meant to replicate transport of CO₂ specifically at the site, historically or modern. Rather, they are designed to address generic questions of reservoir stability in the presence of faults. For example one key difference between these simulations and the evolution of the Springerville site is that the fault did not abruptly open after the CO₂ was emplaced. Another key difference is that CO₂ discharged to the surface along the fault zone at Springerville, whereas in these simulations CO₂ can only move laterally in the shallow groundwater aquifer.

Although this simulation does not mimic actual processes of reservoir development at Springerville, it does provide insights into the mechanisms allowing buoyant CO₂ gas to stay in place despite the presence of vertical leaky conduits. Once the gas within and near the leaky feature escapes to the shallow aquifer, the remaining gas reservoir leaks at a very slow rate. Future studies would be useful for determining the impact of specific factors such as caprock thickness, reservoir thickness, and radial distance to the fault for gas reservoir stability.

8. Conclusions

The CO₂ reservoir at Springerville–St Johns provides a natural analog for understanding mechanisms of long-term CO₂ storage and leakage. Additionally, new insights can be gained regarding

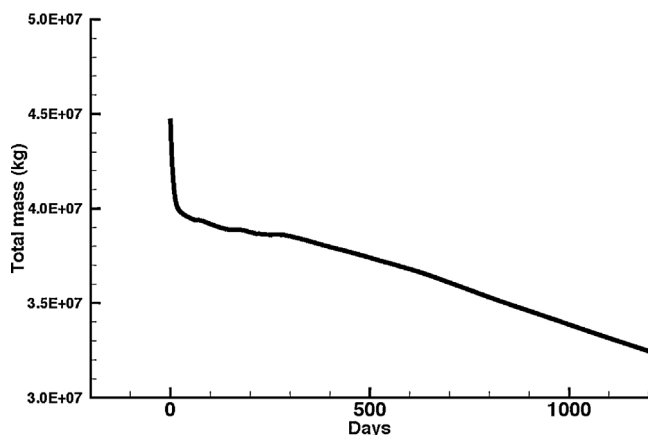


Fig. 12. Total free-phase CO₂ mass in the reservoir (excluding the fault zone).

the impacts of CO₂ leakage on shallow groundwater systems. The primary mechanism of long-term CO₂ storage at this site, and many other natural gas reservoirs has been described previously as ‘solubility trapping’ (Gilfillan et al., 2009). At this site, there appears to be a substantial amount of CO₂ stored in both the dissolved and free (gas) phase (Rauzi, 1999). The simulations here show that buoyant free phase CO₂ can remain at depth despite the presence of a large scale, high permeability leakage path. This is true even when caprock layers are nearly horizontal. This is because, under hydrostatic conditions, there is insufficient driving force for the free phase CO₂ to move laterally toward the fault before it can escape vertically.

Analysis of major, minor element geochemistry and stable isotopes of carbon demonstrates that the leakage pathway (Coyote Wash Fault zone) has been a conduit for upward movement of CO₂ dissolved in brackish or saline water. CO₂ has degassed as the water moved upwards. Possible mechanisms causing upward movement of CO₂-saturated water include: (1) overpressurization at depth due to mantle-derived CO₂ inflow from basement penetrating faults (e.g., Crossey et al., 2009) or (2) groundwater overpressurization due to past glacial to interglacial transitions (e.g., Kampman et al., 2012). Importantly, this differs from the scenario presented by Keating et al. (2010), which considered free phase CO₂ rising along the fault and displacing brine. Here, the primary transport mechanism is upward flow of dissolved phase CO₂.

The measured history of water extraction and consequence pressure declines at a wellfield in the fault zone provided the opportunity to characterize the hydrologic characteristics of the fault zone. Inverse modeling demonstrates that the offset of strata due to faulting is itself sufficient explanation for the hydrologic compartmentalization of TEP monitoring wells to the northeast. However, the fault zone must be broad, permeable, and deep to explain the measured drawdowns given the levels of production over the past few decades. This conclusion does not preclude the possibility that other conceptual models, not tested here, could be equally valid for the site.

Elevated and co-varying concentrations of As, Li, B, Rb, Na, SO₄ and Cl in the shallow aquifer demonstrate some degree of upward transport of brine or brackish water. The fairly linear relationship between trace elements and Cl suggest trace metals were not mobilized in situ due to CO₂ intrusion. This result does not preclude the possibility that this might be the case at other sites. Carbon isotopes suggest that this water was likely saturated with CO₂ and degassed as it moved upward along the fault. As noted by previous authors, the mass rate of CO₂ migrating to the shallow aquifer is presumably much lower than 10's to 100's of thousands of years ago when extensive travertine deposits were created. Salado Springs are currently undersaturated with respect to carbonates (SI, Table 1) and are precipitating travertine today only in small amounts as spring waters degas. Nevertheless, upward transport is still occurring.

There are several possible implications of this study for engineered carbon sequestration and (possible) leakage. First, a breach in the caprock or activated fault may release some CO₂ to the surface but buoyancy alone will not be sufficient to release CO₂ distant from the leakage pathway. Second, the release of CO₂ to the shallow aquifer will not necessarily mobilize trace metals in the shallow aquifer. Our measurements at this site do not support such a mechanism. Third, as previous authors have suggested, mobilization and trapping of CO₂ in the dissolved phase will be the most important process (Gilfillan et al., 2009). At Springerville–St Johns dome, present or past pressure conditions forced brackish or saline water upward along the fault, and with it dissolved CO₂. A significant amount of degassing occurred as the CO₂ rose. These processes are quite different than the conceptual model of buoyancy-driven gas-phase flow in a leakage scenario.

This site could be useful for further field and simulation studies aimed at better understanding CO₂ flow and transport in the subsurface. For example, alternative conceptual models of the site could be tested more rigorously using integrated multi-phase flow/reactive transport simulations and comparison of model results to stable isotope and trace element data. New insights might be gained by sampling a larger number of wells in the area, and analyzing for other trace gases such as helium. Finally, issues related to heterogeneity of fault zones, and impact on CO₂ transport could be explored with focused studies of this site.

References

- Aiuppa, A., Federico, C., Allard, P., Gurrieri, S., Valenza, M., 2005. Trace metal modeling of groundwater–gas–rock interactions in a volcanic aquifer: Mount Vesuvius, Southern Italy. *Chem. Geol.* 216, 289–311.
- Allis, R.G., Moore, J., White, S., 2005. Reactive Multiphase Behavior of CO₂ in Saline Aquifers Beneath the Colorado Plateau. Report to DOE, 23 pp.
- Arizona Department of Water Resources, 2011. Groundwater Site Inventory. <https://gisweb.azwater.gov/waterresourcedata/GWSI.aspx> (2011 retrieval).
- Arizona Department of Water Resources, 2011. Water Atlas. <http://www.azwater.gov/AzDWR/StatewidePlanning/wateratlas/> (2001 retrieval).
- Bills, D.J., Hjalmanson, H.W., Robertson, F.N., 1990. Estimates of Ground-Water Flow Components for Lyman Lake, Apache County, Arizona: U.S. Geological Survey Water-Resources Investigations Report 89-4151, pp. 55.
- Birkholzer, J., Zhou, Q., Tsang, C.-F., 2009. Large-scale impact of CO₂ storage in deep saline aquifers: a sensitivity study on pressure response in stratified systems. *Int. J. Greenhouse Gas Control* 3, 181–194.
- Carey, J.W., Williams, M.R., Hakala, A., Fessenden, J.E., Keating, E.H., 2009. Experimental study of sediment–CO₂ reactions with application to changes in groundwater quality due to leakage of sequestered CO₂. In: American Geophysical Union, Fall Meeting, Abstract, H13A-0913.
- Concha, G., Broberg, K., Grander, M., Cardozo, A., Palm, B., Vahter, M., 2010. High-level exposure to lithium, boron, cesium, and arsenic via drinking water in the Andes of Northern Argentina. *Environ. Sci. Technol.* 44, 6875–6880.
- Condit, C.D., Crumpler, L.S., Aubele, J.C., 1989. Patterns of volcanism along the southern margin of the Colorado Plateau: the Springerville field. *J. Geophys. Res.* 94, 7975–7986.
- Crossey, L.J., Karlstrom, K.E., Springer, A.E., Newell, D., Hilton, D.R., Fischer, T., 2009. Degassing of mantle-derived CO₂ and He from springs in the southern Colorado Plateau region—neotectonic connections and implications for groundwater systems. *GSA Bull.*, <http://dx.doi.org/10.1130/B26394.1>.
- Crumpler, L.S., Aubele, J.C., Condit, C.D., 1994. Volcanoes and Neotectonic Characteristics of the Springerville Volcanic Field, Arizona. New Mexico Geological Society Guidebook, 45th Field Conference, Mogollon Slope, West-Central New Mexico and East-Central Arizona, pp. 147–164.
- Deines, P., Langmuir, D., Harmon, R., 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochim. Cosmochim. Acta* 38, 1147–1164.
- Foust Jr., R.D., Mohapatra, P., Compton-O'Brien, A.M., Reifel, J., 2004. Groundwater arsenic in the Verde Valley in central Arizona, USA. *Appl. Geochem.* 19, 251–255.
- Gilfillan, S.M.V., Ballentine, C.J., Holland, G., Blagburn, D., Sherwood Lollar, B., Stevens, S., Schoell, M., Cassidy, M., 2008. The noble gas geochemistry of natural CO₂ gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA. *Geochim. Cosmochim. Acta* 72, 1174–1198.
- 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. *Int. J. Greenhouse Gas Control* 5, 1507–1516.
- Guilbert, J.M., Park, C.F., 1986. The Geology of Ore Deposits. W.H. Freeman and Company, New York, pp. 985.
- Hoffmann, J.P., Bills, D.J., Phillips, J.V., Halford, K.J., 2006. Geologic, Hydrologic, and Chemical Data from the C Aquifer Near Leupp, Arizona: U.S. Geological Survey Scientific Investigations Report 2005-5280, pp. 42.
- Hovorka, S.D., Benson, S.M., Doughty, C., Freifeld, B.M., Sakurai, S., Daley, T.M., Kharaka, Y.K., Holtz, M.H., Trautz, R.C., Nance, H.S., Myer, L.R., Knauss, K.G., 2006. Measuring permanence of CO₂ storage in saline formations: the Frio experiment. *Environ. Geosci.* 13 (2), 105–121.
- Hovorka, S.D., Meckel, T.A., Trevino, R.H., Lu, J., Nicot, J.-P., Choi, J.-W., Freeman, D., Cook, P., Daley, T.M., Ajo-Franklin, J.B., Freifeld, B.M., Doughty, C., Carrigan, C.R., Brecque, D.L., Kharaka, Y.K., Thordsen, J.J., Phelps, T.J., Yang, C., Romanak, K.D., Zhang, T., Holt, R.M., Lindler, J.S., Butsch, R.J., 2011. Monitoring a large volume CO₂ injection: year two results from SECARB project at Denbury's Cranfield, Mississippi, USA. *Energy Proc.* 4, 3478–3485.
- Johnson, R.H., DeWitt, E., Wirt, L., Manning, A.H., Hunt, A.G., 2012. Using geochemistry to identify the source of groundwater to Montezuma Well, a natural spring in Central Arizona, USA: Part 2. *Environ. Earth Sci.* 67, 1837–1853.

- Kampman, N., Burnside, N.M., Shipton, Z.K., Chapman, H.J., Nicholl, J.A., Ellam, R.M., Bickle, M.J., 2012. Pulses of carbon dioxide emissions from intracrustal faults following climatic warming. *Nat. Geosci.* 5, 352–358.
- Keating, E.H., Newell, D.L., Viswanathan, H., Carey, J.W., Zyvoloski, G., Pawar, R., 2012. CO₂/brine transport into shallow aquifers along fault zones. *Environ. Sci. Technol.* 47 (1), 290–297.
- Keating, E.H. <Et-Al>, 2010. The impact of CO₂ on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration. *Environ. Earth Sci.*, <http://dx.doi.org/10.1007/s12665-009-0192-4>.
- Keating, E.H., Hakala, J.A., Viswanathan, H., Carey, J.W., Pawar, R., Guthrie, G.D., Fessenden-Rahn, J., 2013. CO₂ leakage scenarios: simulations informed by observations at a natural analog site. *Appl. Geochem.* 30, 136–147.
- Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river water across the United States. *Hydrol. Proc.* 15, 1363–1393.
- Kharaka, Y.K., Thordsen, J.J., Kakouros, E., Ambats, G., Herkelrath, W.N., Beers, S.R., Birkholzer, J.T., Apps, J.A., Spycher, N.F., Zheng, L., Trautz, R.C., Rauch, H.W., Gullickson, K.S., 2010. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environ. Earth Sci.* 60, 273–284.
- Kirk, M.F., Holm, T.R., Park, J., Jin, Q., Sanford, R.A., Fouke, B.W., Bethke, C.M., 2004. Bacterial sulfate reduction limits natural arsenic contamination in groundwater. *Geology* 32 (11), 953–956.
- Korbol, R., Kaddour, A., 1995. Sleipner-vest CO₂ disposal – injection of removed CO₂ into the Utsira formation, 1995. *Energy Convers. Manage.* 36 (6–9), 509–512.
- Little, M.G., Jackson, R.B., 2010. Deep CO₂ geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.* 44, 9225–9232.
- Montgomery and Associates, 2011. Hydrogeologic Monitoring Program 2010–201, Springerville Generating Station Area Apache County, Arizona; prepared for Tucson Electric Power.
- Moore, J., Adams, M., Allis, R., Lutz, S., Rauzi, S., 2005. Mineralogical and geochemical consequences of the long-term presence of CO₂ in natural reservoirs: an example from the Springerville–St. Johns Field, Arizona, and New Mexico, U.S.A. *Chem. Geol.* 217, 365–385.
- Newell, D.L., Jessup, M.J., Cottle, J.M., Hilton, D., Sharp, Z., Fischer, T., 2008. Aqueous and isotope geochemistry of mineral springs along the southern margin of the Tibetan plateau: implications for fluid sources and regional degassing of CO₂. *Geochim. Geophys. Geosyst.* 9, Q08014, <http://dx.doi.org/10.1029/2008GC002021>.
- Oldenburg, Curtis, M., Rinaldi, A.P., 2011. Buoyancy effects on upward brine displacement caused by CO₂ injection. *Trans. Porous Med.* 87, 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: USGS Water-Resources Investigations Report 99-4259, pp. 310.
- 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. *Environ. Earth Sci.* 7 (2), 335–349.
- Preisig, M., Prevost, J.H., 2011. Coupled multi-phase thermo-poromechanical effects. Case study: CO₂ injection at In Salah, Algeria. *Int. J. Greenhouse Gas Control* 5 (4), 1055–1064.
- Rauzi, S., 2003. Review of Helium Production and Potential in Arizona, Open-File Report 03-05. Arizona Geological Survey, 30 pp.
- Rauzi, S., 1999. Carbon Dioxide in the St. Johns–Springerville Area, Apache County, Arizona. Open-File Report 99-2. Arizona Geological Survey, 24 pp.
- Risacher, F., Fritz, B., 1991. Quaternary geochemical evolution of the salars of Uyuni and Coipasa, Central Altiplano, Bolivia. *Chem. Geol.* 90, 211–231.
- Sharp, Z.D., 2006. Principles of Stable Isotope Geochemistry. Pearson/Prentice Hall, Upper Saddle River, NJ, pp. 344.
- Smyth, R.C., Hovorka, S.D., Lu, J., Romanak, K.D., Partin, J.W.C., Yang, W.C., 2009. Assessing risk to fresh water resources from long term CO₂ injection-laboratory and field studies. *Energy Proc.* 1, 1957–1964.
- Stevens, S.H., Fox, C., White, T., Melzer, S., 2005. Natural CO₂ Analogs for Carbon Sequestration. Final Report for DOE.
- Trautz, R.C., Pugh, J.D., Varadharajan, C., Zheng, L., Bianchi, M., Nico, P.S., Spycher, N.F., Newell, D.L., Esposito, R.A., Wu, Y., Dafflon, B., Hubbard, S.S., Birkholzer, J.T., 2013. Effect of dissolved CO₂ on a shallow groundwater system: a controlled release field experiment. *Environ. Sci. Technol.* 47, 298–305.
- Zyvoloski, G.A., 1997. Summary of the Models and Methods for the {FEHM} Application – A Finite-Element Heat- and Mass-Transfer Code; Los Alamos National Laboratory Report, 72 pp.