

Geochemical variability in an active CO₂-enhanced oil recovery reservoir and overlying groundwater

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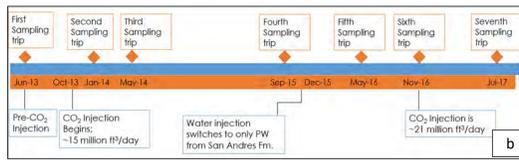
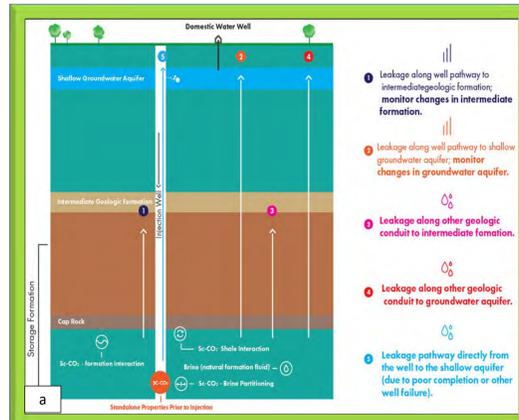


Introduction

Permanent storage of CO₂ relies on preventing CO₂ migration via various pathways to overlying formations (Fig. 1a). CO₂ enhanced oil recovery fields provide an opportunity to monitor for these leakage pathways in real time and to observe how produced waters change during standard field practices for CO₂-injection.

This research focuses on long term monitoring (Fig. 1b) of produced waters and overlying groundwaters at an active CO₂-enhanced oil recovery field. The geochemistry of produced waters can provide insight into how injected CO₂ affects reactions within a producing formation. Simultaneous groundwater sampling establishes a baseline time series to characterize geochemical variability in groundwater signals for monitoring of CO₂ storage sites.

Produced water (Permian San Andres Fm.) and overlying groundwater samples (Triassic Santa Rosa Fm. and Miocene Ogallala Fm.) were taken from the Permian Basin's Central Basin Platform during a 4-year period from June 2013 to July 2017, bracketing the onset of carbon dioxide injection. Produced water and groundwaters were measured for field parameters (pH, TDS, alkalinity), major geochemical analytes (Ca, K, Mg, Na, SO₄, Cl), and multiple isotope systems ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$).



System	Series	Central Basin Platform Group/Formation	Lithology	Average Depth (m) of Samples at field area	Hydrostratigraphic Unit
Quaternary	Upper	Ogallala	Fluvial and lacustrine clastics	~45-55	Evaporite Confining System
	Lower	Fredericksburg	Limestone		
Cretaceous	Albian	Archer / Paluxy	Sandstone		Evaporite Confining System
	Albian	Archer / Paluxy	Sandstone		
Triassic	Upper	Dockum Group / Santa Rosa Fm.	Fluvial-deltaic and lacustrine clastics	~460	Evaporite Confining System
	Lower	Dockum Group / Santa Rosa Fm.	Fluvial-deltaic and lacustrine clastics	~460	
Permian	Ochoan	Denney Lake	Halite, Anhydrite, Sphite		Deep Basin Aquifer System
	Ochoan	Bluffton			
	Ochoan	Salsado			
	Ochoan	Tanhill			
	Ochoan	Yates			
	Ochoan	Seven Rivers	Sandstone and Anhydrite		
	Ochoan	Queen			
	Ochoan	Grayburg			
	Ochoan	Upper San Andres	Dolomite	~1630	
	Ochoan	Lower San Andres			
Leonardian	Holt			Deep Basin Aquifer System	
	Gossard				
	Clear Fork Group	Limestone and Dolomite			
	Wichita				
Wolfcampian	Wolfcamp	Shale, carbonates		Deep Basin Aquifer System	

Figure 1. (a) Cross section illustrating various flow pathways at a carbon storage site, (b) time-line of project sampling events, and (c) generalized strat. section of field area with sampled formations highlighted. Fig. 1c is modified from Engle et al., 2016 and Pfister et al., 2017

Methods

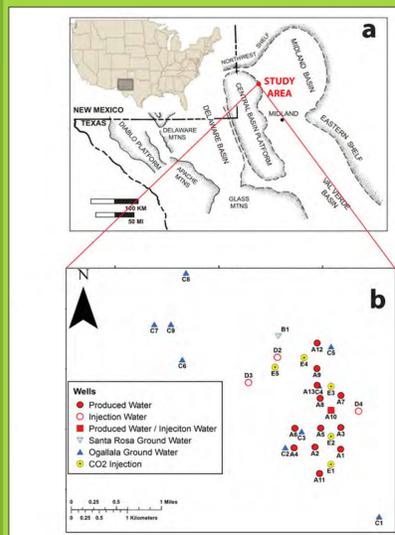


Figure 2. (a) Location of field area in the Permian Basin (b) distribution of sampled wells.

Water samples were taken from an oil field in the Permian Basin's Central Basin Platform on seven different sampling trips over a four-year period (June 2013-July 2017). At the field site, produced water samples (n=13) were taken from the San Andres (~1630 m) and groundwater samples were taken from shallow (n=9; Ogallala, ~45-55 m) and deep (n=1; Santa Rosa, 460 m) aquifers (Fig. 2a). Injection water samples (n=4) were also taken at this site.

Produced waters and injection waters were collected in 2 gallon-plastic containers fitted with a cap and a bottom spigot and were allowed to settle for a time period (~1-24 hours) during which the oil, paraffin, and water separated to yield relatively oil free water samples out of the bottom spigot. This oil-water separate was then filtered serially through a packed cartridge of glass wool and then a 0.45 μm high capacity filter without exposure to air.



Figure 3. (a) Pump jack at field site, (b) researchers separating produced waters, and (c) researchers sampling groundwater from irrigation wells proximal to field site.

All fresh groundwater samples were collected in clean, unused 2 gallon-plastic containers. Some field measurements (pH and TDS) were measured at the well head using unfiltered sample. The groundwaters were filtered using only a 0.45 μm EnviroTech high capacity cartridge filter. Aliquots were taken for isotope systems ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$) and for ion analyses for both produced water and groundwater samples.

Results & Discussion

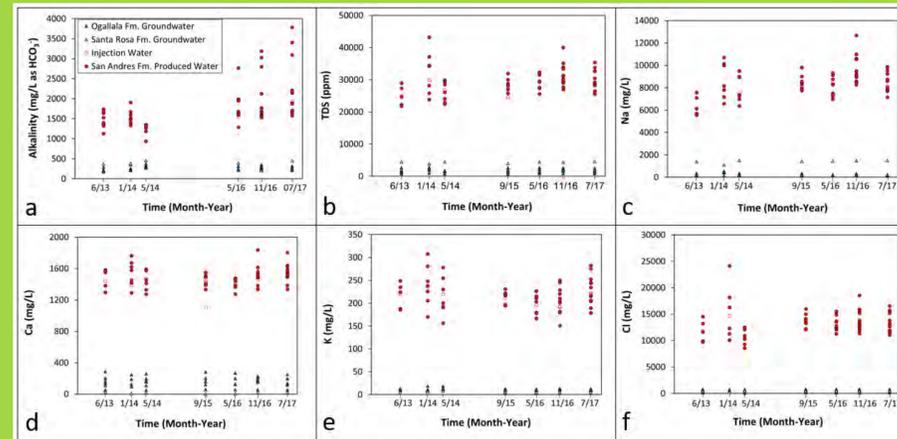


Figure 4. Selected analytes for groundwaters and produced waters, including (a) alkalinity, (b) total dissolved solids (TDS), (c) sodium, (d) calcium, (e) potassium, and (f) chloride. Produced waters display significant increases in alkalinity, TDS, and sodium after CO₂ injection began.

Several measurements (alkalinity, TDS, Ca, K, Na, and Cl) from the San Andres produced waters occupy distinctive ranges relative to overlying groundwaters (Fig. 4a-f). San Andres produced waters exhibit a much higher range (63,500-76,500 ppm) of TDS measurements (Fig. 4b) than either the Santa Rosa groundwater range (3,860-4,580 ppm) or the Ogallala groundwater range (550-2,700 ppm). Although other analytes also display large discrepancies (Fig. 4a,c-f), certain analytes (Mg, SO₄) produce results that are proximal to those from overlying groundwaters. While these large discrepancies would be expected between a produced water and a groundwater, it is important to identify that these analytes are more sensitive indicators of produced water intrusion than other general geochemical parameters at this site. These more sensitive general geochemical parameters are relatively stable in observed groundwaters, suggesting that CO₂ injection activities did not cause migration of produced water into overlying groundwaters.

Following the onset of CO₂ injection, produced waters displayed significant increases in alkalinity, total dissolved solids, and sodium values relative to the pre-CO₂ injection sampling period (Fig 4a-c). While alkalinity values initially fluctuated post-injection, the final three sampling trips display markedly higher median and maximum values relative to the pre-injection sampling event in June 2013 (Fig. 4a). The increase in alkalinity could be due to injected CO₂ dissolving into the produced water or enhanced dissolution of the surrounding dolomite reservoir, although there are no observed increases in dissolved Ca or Mg. An increase in alkalinity following CO₂-injection, specifically in carbonate hosted groundwaters, has been documented in previous research (Kharaka et al., 2010). This alkalinity increase can coincide with a pH-decrease at reservoir pressures.

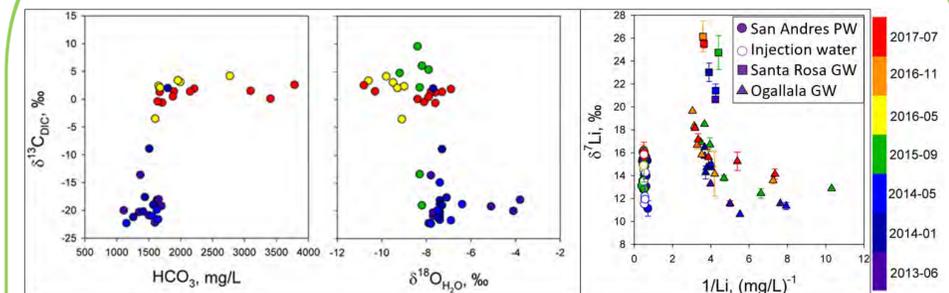


Figure 5. Carbon isotope, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of San Andres produced water; $\delta^7\text{Li}$ of produced water and groundwater.

CO₂ injection operations produced a shift in produced water signatures for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Fig 5). This shift suggests that the injected CO₂ became the primary source of dissolved inorganic carbon within the producing reservoir. Groundwater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ did not exhibit such a similar shift, suggesting that injected CO₂ was not leaking into the overlying groundwaters. $\delta^7\text{Li}$ data do not exhibit a noticeable shift during CO₂ injection (Fig. 5). Although Ogallala groundwater and San Andres produced water have similar $\delta^7\text{Li}$ ranges, Santa Rosa groundwater has a unique $\delta^7\text{Li}$ signature relative to sampled produced water, indicating it could be sensitive to intrusion of produced water at this site.

CO₂ injection activity does not appear to affect $^{87}\text{Sr}/^{86}\text{Sr}$ values in either the producing formation or overlying groundwaters (Fig. 6). Both groundwaters have relatively distinct $^{87}\text{Sr}/^{86}\text{Sr}$ signatures relative to the underlying produced water, suggesting that $^{87}\text{Sr}/^{86}\text{Sr}$ would be an early indicator of produced water intrusion in both the intermediate and shallow groundwaters.

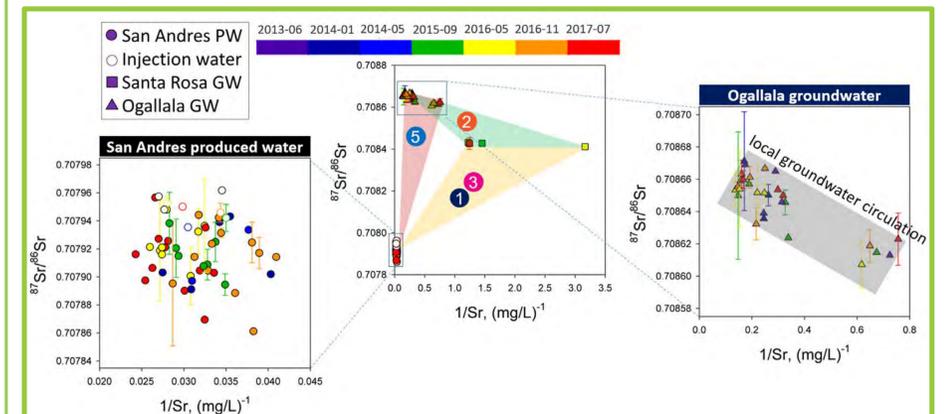


Figure 6. $^{87}\text{Sr}/^{86}\text{Sr}$ of site produced waters and groundwaters; numbers in central figure refer back to leakage pathways displayed in Fig. 1a.

Conclusions

- CO₂ injection has easily observable effects on alkalinity, total dissolved solids and sodium values in produced waters in the carbonate reservoir.
- Only some groundwater parameters are distinct and therefore useful to constrain pathways of leakage between produced water and overlying groundwater
- No evidence of intrusion of produced water into overlying groundwaters was observed throughout the study. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values can indicate presence of injected CO₂. $^{87}\text{Sr}/^{86}\text{Sr}$ are a more versatile indicator of brine intrusion at this site than $\delta^7\text{Li}$.

References

Engle, M.A., Reyes, F.R., Varonka, M.S., Orem, W.H., Ma, L., Ianno, A.J., Schell, T.M., Xu, P. and Carroll, K.C., 2016. Geochemistry of formation waters from the Wolfcamp and "Cline" shales: Insights into brine origin, reservoir connectivity, and fluid flow in the Permian Basin, USA. *Chemical Geology*, 425, pp.76-92.

Kharaka, Y.K., Thordson, J.J., Kakouros, E., Ambats, G., Herkelrath, W.N., Beers, S.R., Birkholzer, J.T., Apps, J.A., Spycher, N.F., Zheng, L. and Trautz, R.C., 2010. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana. *Environmental Earth Sciences*, 60(2), 273-284.

Pfister, S., Capo, R.C., Stewart, B.W., Macpherson, G.L., Phan, T.T., Gardiner, J.B., Diehl, J.R., Lopano, C.L. and Hakala, J.A., 2017. Geochemical and lithium isotope tracking of dissolved solid sources in Permian Basin carbonate reservoir and overlying aquifer waters at an enhanced oil recovery site, northwest Texas, USA. *Applied Geochemistry*, 87, 122-135.

Acknowledgments

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