

Article

Chemical Impacts of Potential CO₂ and Brine Leakage on Groundwater Quality with Quantitative Risk Assessment: A Case Study of the Farnsworth Unit

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Abstract: Potential leakage of reservoir fluids is considered a key risk factor for geologic CO₂ sequestration (GCS), with concerns of their chemical impacts on the quality of overlying underground sources of drinking water (USDWs). Effective risk assessment provides useful information to guide GCS activities for protecting USDWs. In this study, we present a quantified risk assessment case study of an active commercial-scale CO₂-enhanced oil recovery (CO₂-EOR) and sequestration field, the Farnsworth Unit (FWU). Specific objectives of this study include: (1) to quantify potential risks of CO₂ and brine leakage to the overlying USDW quality with response surface methodology (RSM); and (2) to identify water chemistry indicators for early detection criteria. Results suggest that trace metals (e.g., arsenic and selenium) are less likely to become a risk due to their adsorption onto clay minerals; no-impact thresholds based on site monitoring data could be a preferable reference for early groundwater quality evaluation; and pH is suggested as an indicator for early detection of a leakage. This study may provide quantitative insight for monitoring strategies on GCS sites to enhance the safety of long-term CO₂ sequestration.

Keywords: geologic CO₂ sequestration; CO₂ and brine leakage; underground source of drinking water; risk assessment; response surface methodology; early detection criteria

1. Introduction

Carbon dioxide capture and sequestration (CCS) in geologic formations is considered a promising approach for mitigating CO₂ emissions, by injecting CO₂ from stationary sources into deep geologic formations [1,2]. After the policy of United States emphasized “utilization” of carbon capture, utilization, and storage (CCUS), CO₂-enhanced oil recovery (CO₂-EOR) and storage has gained specific interest for its potential benefits of increasing oil production and reducing CO₂ storage costs [3–5].

It is believed that the risks of geologic CO₂ sequestration (GCS) to the environment and human health are minimized with monitoring and managements of the sites, especially for operational reservoirs with pressure managements [6–8]. However, the concern of reservoir fluids, especially CO₂ leakage to overlying underground sources of drinking water (USDWs) cannot be completely ruled out [9–12]. Carbon dioxide itself is not hazardous to groundwater quality, but it triggers pH reduction, water-sediment interactions, and potential toxic trace metal release from sediments [13–15]. Reservoir

brine leakage may significantly increase shallow groundwater salinity and introduce hazardous reservoir substances into overlying USDWs [16,17].

Wells are usually identified as a greater risk of potential leakage pathways than geological features of faults and/or fractures [18,19]. Specifically, reservoir fluids may leak through wellbore cement and well casing. Wellbore cement degradation caused by CO₂ intrusion is a complex function of cement properties, fluid dynamics, reaction kinetics, and stress state of the wellbore environment [20–23]. It is believed that moderate exposure to CO₂ could provide a less permeable front of the cement with calcite precipitation to avoid further acid intrusion for centuries [19,21,24,25]. Even with microcracks occurring in wellbores, most leaked CO₂ could be trapped by the cement, and leakage flux of reservoir fluids (CO₂ and brine) is neglectable to be considered as a potential risk [26]. In most risk assessment studies, abandoned legacy wells with hypothetical open boreholes and/or wellbore failures are assumed as the most likely leakage pathways [27,28]. It represents the worst-case scenario for area of review (AoR) evaluations stipulated by the U.S. Environmental Protection Agency (EPA) Underground Injection Control (UIC) guidance, where wells with stability problems, casing failure, and/or abandoned wells not identified with site characterization and monitoring approaches [27]. Maximum CO₂ leakage rates between 10⁻⁷ and 10⁻¹ kg/s are used for most risk assessment approaches, which is usually up to 0.4% of the cumulative CO₂ injected in the reservoir [27,29,30].

Regulatory policy emphasizes the protections against reservoir leakage to USDWs with assessments of risks to water quality for the USDWs and groundwater monitoring prior to, during, and after injection phases [8]. To date, quantitative risk assessments of modeling approaches combined with field observations play an essential role for site-specific studies of potential leakage and its impact on USDW quality, to forecast the long-term response of groundwater, and help the operators to make effective and efficient plans of monitoring strategies [26,27,31–33]. Monte Carlo method is a straightforward simulation approach for risk assessment [34], but its high computational cost motivates the applications of reduced order models (ROMs) to replace original simulations with surrogate models [35]. Response surface methodology (RSM) is a widely-used statistical and mathematical technique to generate ROMs, and has been applied for many risk assessment approaches for GCS research [26,34,36]. Thus, RSM was selected to quantify risks on shallow groundwater quality in this study.

In this manuscript, we present quantitative assessment of potential risks to overlying groundwater quality due to CO₂ and brine leakage at an on-going CO₂-EOR and storage site, the Farnsworth Unit (FWU). Considerable operational, geological, and geochemical data available of the reservoir and the overlying USDW aquifer (the Ogallala aquifer) largely improved the reliability with reduced uncertainties. Specific objectives include: (1) to quantify potential risks to the overlying USDW quality due to CO₂ and brine leakage from the operational reservoir; and (2) to identify water chemistry indicators for early detection criteria. Results of this study may provide a useful perspective of combining numerical simulations, field observations, and ROMs for site-specific risk assessments to enhance the safety of GCS projects.

2. Materials and Methods

2.1. Site Description

The FWU site (Figure 1) located in northern Texas is a mature hydrocarbon reservoir undergoing active CO₂-EOR and sequestration since December 2010 [37,38]. It is the study site of the Southwest Regional Partnership on Carbon Sequestration (SWP) Phase III, sponsored by the U.S. Department of Energy (DOE) and the National Energy Technology Laboratory (NETL) [39]. The primary goal of this project is to exhibit and evaluate an active commercial-scale CCUS operation, and demonstrate effective site characterization, monitoring, verification, accounting, and risk assessment for long-term CO₂ sequestration. To date, over one million metric tons of net CO₂ from anthropogenic sources (one fertilizer plant and one ethanol plant) is stored in the subsurface reservoir (the Morrow B Formation), with CO₂ injection and production volumes tracked at the FWU [40]. The SWP acquired significant

near-surface monitoring data for potential CO₂ leakage, including soil CO₂ flux (to identify any potential point-source leakage to the surface), borehole CO₂ movement (to monitor subsurface CO₂ movement), and the overlying drinkable groundwater chemistry in the Ogallala aquifer (to identify any potential leakage into the USDW and drinking water quality change). The SWP project partner, the National Institute of Advanced Industrial Science and Technology (AIST) of Japan conducted surface/shallow borehole gravity and electrical methods to monitor the subsurface CO₂ plume [41]. Continuous gravity, self-potential, and magnetotelluric surveys were also applied for three years to monitor brine leakage into the Ogallala aquifer. Up to date, these monitoring activities have not seen any CO₂/brine leakage [39], and the monitoring data along with reservoir characterization provide essential information to improve the reliability of risk assessment at the site.

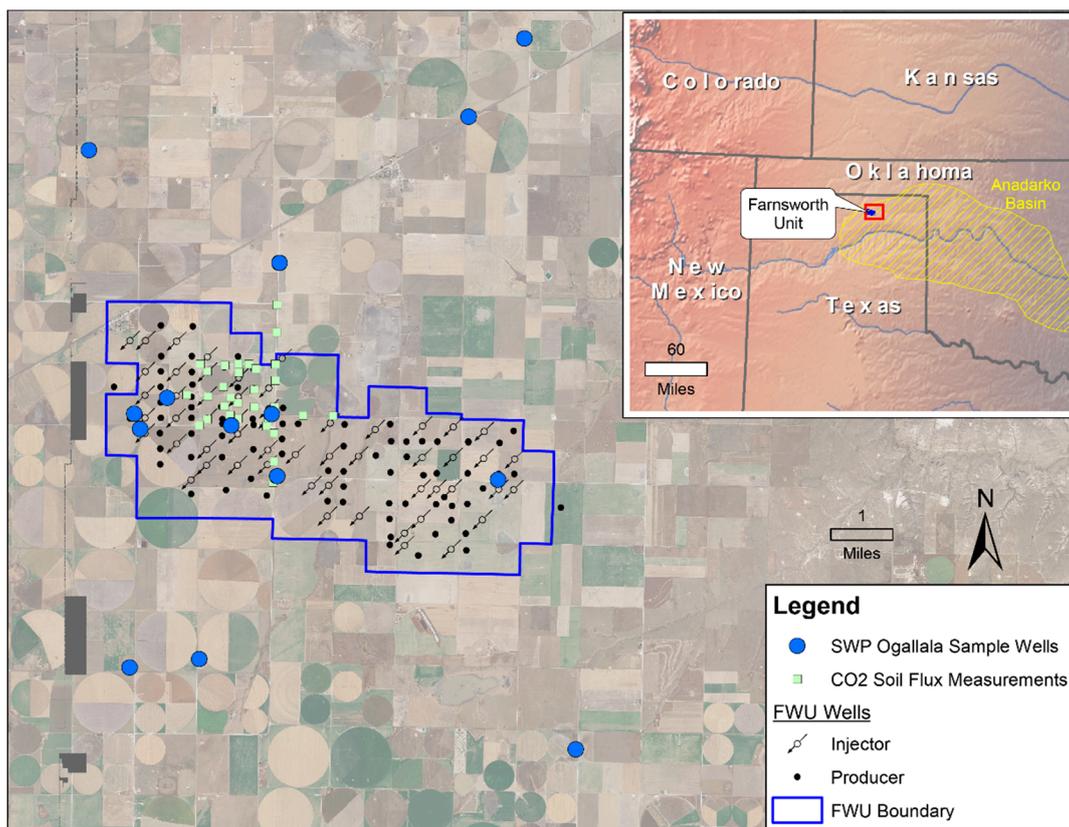


Figure 1. The Farnsworth Unit (FWU) location with 5-patterns of CO₂ injection and oil production, and monitoring locations for CO₂ leakage to the groundwater and surface.

2.2. Site-Specific Water Chemistry and No-Impact Thresholds

On-site monitoring water chemistry provides reliable baseline of shallow groundwater and reservoir brine constituents and determines the potential risks of exceeding water quality thresholds due to any potential CO₂ and/or brine leakage. To date, there are hundreds of water samples collected and analyzed in quarterly basis from the Ogallala aquifer and the reservoir at the FWU area since 2012, conducted by the New Mexico Institute of Mining and Technology, as part of SWP Phase III. General chemistry was analyzed for pH (by pH meter), conductivity (by conductivity meter), alkalinity (by electrometric titration), oxidation and reduction potential (ORP, by pH meter and ORP electrode), major cations and anions (including Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, Br⁻, NO₃⁻, and SO₄²⁻, by ion chromatography (IC)), trace metals (by inductively coupled plasma mass spectrometry (ICP-MS)), inorganic carbon (IC), and non-purgeable organic carbon (NPOC, by total organic carbon (TOC) analyzer), and total dissolved solids (TDS, calculated based on the concentrations of major cations and anions [42]). Table 1 summarizes selected monitored water parameters of the Ogallala aquifer

and the reservoir produced water. These selected parameters might exceed the U.S. Environmental Protection Agency (EPA) and/or local primary and secondary maximum contaminant levels (MCL) in the Ogallala aquifer with CO₂ and/or brine leakage. Some of the selected contents are sensitive to CO₂ introduction (e.g., pH and trace metals), and some of the contents' concentrations might increase with leaked brine (e.g., TDS and Mn). Changes of these contents may become indicators for any potential leakage as an early-detect criterion.

Table 1. Selected Water Chemistry of the Ogallala Aquifer and the reservoir produced water (PW), maximum contaminant levels (MCL) of the U.S. Environmental Protection Agency (EPA) and Texas State, and No-Impact Threshold (NIT) for potential contaminants of the Ogallala aquifer (unit in mg/L, pH unitless).

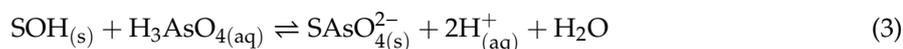
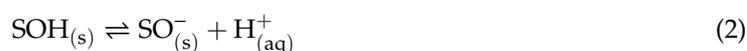
Name	Ogallala	PW	EPA MCL	Texas MCL	NIT
pH	7.7	7.2	6.5	7.0	7.5
Total dissolved solids (TDS)	380	4064	500	1000	508
Mn	0.008	0.27	0.05	0.05	0.05
As	0.003	0.005	0.01	0.01	0.005
Se	0.004	0.07	0.05	0.002	0.007

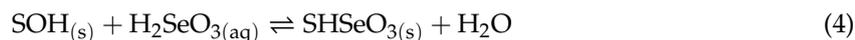
Usually MCLs are used to evaluate whether a leakage plume is harmful for shallow groundwater quality—if the concentration exceeds the limit it would be considered as a risk [17,43,44]. However, the regulatory limits do not reflect the changes from the current background levels at a specific area, especially when a constituent background concentration is significantly lower than the MCL [45]. To determine statistically significant changes of the groundwater for site-specific early detection criteria, the “no-impact thresholds” are defined to predict potential impacts of the leakage in the early stage [45]. The no-impact thresholds are based on site-specific groundwater quality data, and represent the lowest detectable concentrations above the “no change” scenario to predict groundwater quality changes due to any leakage [27,45]. The no-impact thresholds are calculated as the 95%-confidence, 95%-coverage tolerance limit from the existing site monitoring data, and, in some cases, the values might be significantly different from the regulatory standards.

Both no-impact and MCL thresholds were considered in our risk assessments for chemical impacts of groundwater at the FWU [26]. pH, TDS, arsenic (As), selenium (Se), and manganese (Mn) were selected as potential key factors to indicate water quality changes and early detection criteria, where pH directly decreases with CO₂ intrusion, trace metals (As and Se) exist in the reservoir brine and may release from the shallow aquifer sediment at lower pH; TDS and Mn are with high concentrations in the brine, and CO₂-water interactions also change TDS with mineral dissolution.

2.3. Trace Metal Mobilization Due to CO₂ Leakage

Increased CO₂ concentrations in shallow groundwater aquifers would reduce water pH and enhance water-sediment geochemical reactions, resulting in mobilization of toxic trace metals [9,13,43,46–48]. Adsorption/desorption is considered the major mechanism of trace metal release [17,49–51], and it was also considered in our study. The widely used Gouy–Chapman double diffuse layer surface complexation model was applied in our simulations, to calculate such processes [52]. Adsorption/desorption reactions (take As and Se as examples) of sorbent minerals (*S* represents mineral sites) could be written as [49,53]:





Hydrous ferric oxide (HFO) and clay minerals (e.g., kaolinite, illite, and smectite) are often used as a sorbent for simulations of trace metal adsorption in groundwater aquifers, because of their large surface areas and occurrence in natural system [52,53]. Adsorption reactions are controlled by the total amount of sorption sites, which is controlled by the amount of sorbent, site density, and sorbent surface area [54]. It is often difficult to quantify the fractions and/or determine their surface areas because of their low concentrations in the sediments, the minerals playing the role of sorbent are usually assumed with a small volume fraction in simulations and treated as an uncertainty parameter in risk assessment [17,26,54]. The X-ray diffraction (XRD) results of the Ogallala aquifer sediments collected at the FWU area suggested a trace amount of smectite in the samples (< 1% of the aquifer sediment). Therefore, the sorbent amount of the Ogallala sediment was treated as an uncertainty parameter in our assessments for trace metal mobilizations by assuming a fixed sorbent fraction with changing its surface area as an uncertainty parameter.

2.4. Quantification Risk Assessment of Groundwater Quality

2.4.1. Response Surface Methodology (RSM)

Chemical impacts of CO₂ leakage into the Ogallala aquifer in our case study was conducted with RSM, a statistical and mathematical technique for improving and optimizing model exploitation based on a largely reduced number of numerical simulations compared to traditional approaches (e.g., Monte Carlo method) [36]. Stages of RSM application include: (1) determining independent uncertainty parameters and numerical simulation design; (2) conducting simulations according to the selected experimental matrix to train the RSM model equation; (3) obtaining the RSM model equation (a polynomial function) and evaluating the model adequacy; and (4) using the RSM model equation to quantify the risks.

CO₂ and brine leakage rates, aquifer thickness, and adsorbent amount were selected as independent variables in this study (Table 2), because they are controlling variables to determine the leakage plume and water chemistry changes in the USDW aquifer. A conceptual well with failure was assumed for reservoir leakage, and 0.4% of CO₂ and water injection rates were assigned for the maximum leakage rates based on injection history of Well 13-9 in the FWU [55], following the typical leakage rate ranges of previous risk assessment approaches [27]. The Ogallala aquifer thickness range and distribution were assigned based on ~150 shallow groundwater well-drilling data at the FWU area, with average thickness 120 m. The adsorbent amount of the Ogallala sediment was treated as an uncertainty parameter by varying its specific surface area (SSA) with a fixed (assumed) sorbent volume fraction of 0.5% smectite. Box–Behnken design was applied with 25 simulations in total (Table 3) [56]. Regional groundwater flow was neglected in this study for simplicity, because the regional hydraulic gradient (~10 m/year) is low for significant impacts on contamination dilution [26].

Table 2. Independent Parameters for response surface methodology (RSM) of CO₂ and Brine Impacts to the Groundwater. SSA, specific surface area.

Parameter Name	Low (−1)	Mid (0)	High (+1)	Distribution
CO ₂ leakage rate: g/s	0	0.5	1.0	Uniform
Brine leakage rate: g/s	0	0.25	0.5	Uniform
Aquifer thickness: m	40	120	200	Normal
Adsorbent SSA: m ² /g	1	50.5	100	Uniform

Table 3. Box–Behnken experimental design for the reactive transport simulations. Low (−1), mid (0), and high (+1) values are corresponding to the values and order of independent parameters shown in Table 2.

Simulation	Values of Independent Parameters				Simulation	Values of Independent Parameters			
1	−1	−1	0	0	14	0	−1	1	0
2	−1	1	0	0	15	0	1	−1	0
3	1	−1	0	0	16	0	1	1	0
4	1	1	0	0	17	−1	0	−1	0
5	0	0	−1	−1	18	−1	0	1	0
6	0	0	−1	1	19	1	0	−1	0
7	0	0	1	−1	20	1	0	1	0
8	0	0	1	1	21	0	−1	0	−1
9	−1	0	0	−1	22	0	−1	0	1
10	−1	0	0	1	23	0	1	0	−1
11	1	0	0	−1	24	0	1	0	1
12	1	0	0	1	25	0	0	0	0
13	0	−1	−1	0					

2.4.2. Reactive Transport Model

A one-dimensional conceptual radial model (Figure 2) was assembled and simulated to analyze the potential risks to groundwater quality due to CO₂ and brine leakage. The model radius was assigned 10,000 m (significantly far from the potential leaky well) with 80 cells. A constant temperature of 25 °C was assigned with homogeneous porosity of 0.3 and permeability 10^{−13} m², according to the characterizations of the aquifer. With consideration of CO₂ injection for at least 30 years, and a 50-year post-monitoring period required for a GCS project after CO₂ injection is ceased, the total simulation time was arbitrarily assigned 200 years, which was significantly longer than the injection and post-injection (monitoring) period (~75 years in total).

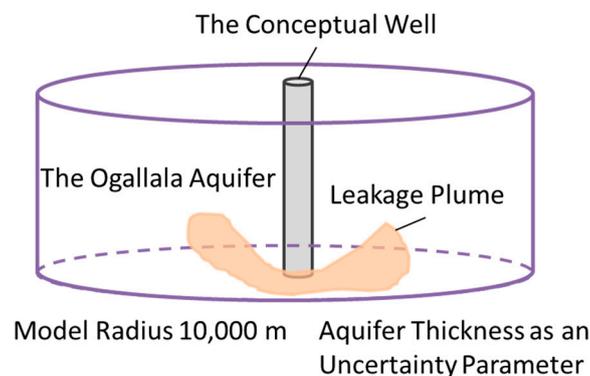


Figure 2. The conceptual model for the Ogallala Aquifer.

The initial groundwater and leakage brine chemistry for the model was assigned based on the average composition of the FWU monitoring samples (Table 4). The initial mineralogy was assigned following the XRD results of the Ogallala sediment samples collected at the FWU area (Table 5), with mineral reactive surface areas assigned following literature [17,55]. Aqueous complexation, cation exchange (Na⁺, H⁺, Ca²⁺, Mg²⁺, K⁺, Fe²⁺, and Mn²⁺), adsorption/desorption and mineral dissolution/precipitation were considered for chemical reactions in the aquifer. The thermodynamic parameters for aqueous and mineral reactions were assigned following the EQ3/6 database [57]. The parameters for the kinetic rate law of minerals were taken from [58]. The Gouy–Chapman double diffuse layer model was used for adsorption reactions [53,59]. Cation exchange coefficients were taken from [60]. All simulations were performed with TOUGHREACT V2 [61] and with equation of state ECO2N for multiphase CO₂ and brine [62].

Table 4. Initial water chemistry for the Ogallala Aquifer and the leaked reservoir brine (PW) (unit: mol/kg).

Name	Ogallala	PW	Name	Ogallala	PW
pH (unitless)	7.7	7.2	SiO ₂ (aq)	6.613×10^{-4}	6.667×10^{-4}
Ca ²⁺	1.189×10^{-3}	1.937×10^{-3}	Cl ⁻	1.582×10^{-3}	5.619×10^{-2}
Mg ²⁺	7.935×10^{-5}	1.286×10^{-4}	HCO ₃ ⁻	2.355×10^{-3}	4.267×10^{-3}
Na ⁺	2.068×10^{-3}	6.407×10^{-2}	SO ₄ ²⁻	5.105×10^{-4}	2.735×10^{-4}
K ⁺	2.649×10^{-4}	4.534×10^{-4}	NO ₃ ⁻	2.399×10^{-4}	3.898×10^{-6}
Fe ²⁺	8.880×10^{-9}	6.517×10^{-9}	H ₂ AsO ₄ ⁻	5.290×10^{-9}	6.775×10^{-8}
AlO ₂ ⁻	2.311×10^{-10}	1.732×10^{-10}	HSeO ₃ ⁻	1.733×10^{-8}	8.887×10^{-6}
Mn ²⁺	1.457×10^{-7}	4.568×10^{-6}			

Table 5. Initial mineralogy assigned for the model. Mineral surface areas are assigned following literatures [17,55].

Mineral Name	Formula	Volume Fraction	Surface Area (cm ² /g)
Primary			
Quartz	SiO ₂	0.780	23.29
Calcite	CaCO ₃	0.110	53.96
K-Feldspar	KAlSi ₃ O ₈	0.092	222.42
Dolomite	CaMg(CO ₃) ₂	0.004	9.80
Smectite	Na _{0.29} Mg _{0.26} Al _{1.77} Si _{3.97} O ₁₀ (OH) ₂	0.005	151.60
Albite	NaAlSi ₃ O ₈	0.005	11.40
Secondary			
Illite	K _{0.6} Mg _{0.25} Al _{1.8} (Al _{0.5} Si _{3.5} O ₁₀)(OH) ₂	0	272.06

3. Results and Discussion

3.1. Impacts on Groundwater Quality

The RSM model equations of our target parameters were trained with 25 numerical simulations. Overall, the correlation between the original (full reservoir model) simulated results and the RSM forecasted results are above 0.9 for most of the grids, especially within 100 m from the conceptual well, suggesting that the trained RSM equations (polynomial functions) sufficiently fit the original reactive transport model outcomes and are adequate for forecasting the water quality parameters of interest within the selected range. With the trained polynomial RSM equations, selected parameters were calculated with 10,000 random cases (each independent variable was created with a random seed in their selected ranges). Cumulative distribution functions (CDF) were obtained accordingly, and they were used for forecasting the likelihood that the leakage would impact groundwater quality over 200 years.

Figure 3 illustrates CDFs of gaseous CO₂ saturation (SG) within 50 m radius away from the conceptual leaky well in the aquifer. If CO₂ leaked through a well with a maximum leakage rate of 1 g/s, it is very likely that gaseous phase CO₂ be observed in the aquifer 1 m away from the well after 1 year, and the plume radius increases to 10 m after 10 years. With the gas phase CO₂ intrusion, pH of the aquifer decreases accordingly, and local groundwater might drain off near the well. TDS concentration near the well might become extremely high with the worst scenarios due to CO₂ dissolution as well as the leaked brine contribution (Figure 4). It is less likely for gaseous CO₂ plume reaching 50 m away from the conceptual well within 100 years, and at the 200th year, cases above the 60th percentile show a small amount of free gas at this distance. It is likely that the free gas plume would reach 50 m away from the well after 200 years' leakage. With the maximum leakage rate of 0.4% injection rate, none of the simulations show an occurrence of gas phase CO₂ at the location 100 m away from the well.

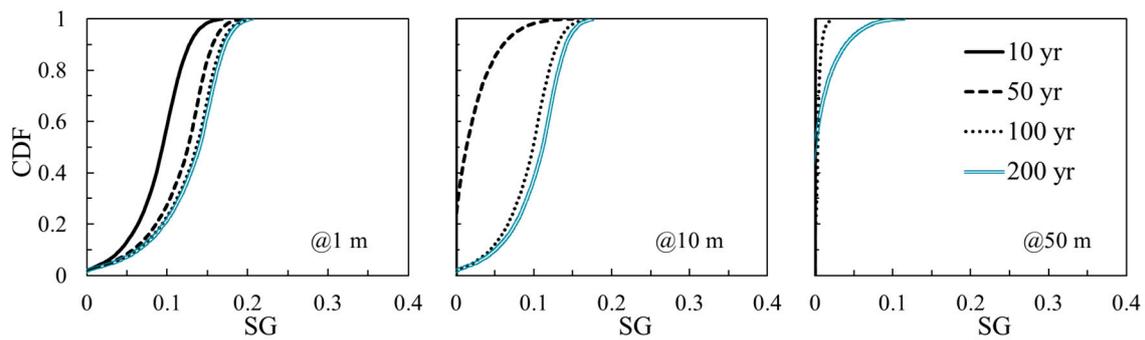


Figure 3. Cumulative distribution functions (CDFs) of gaseous phase CO₂ Saturation (SG) at 1 m, 10 m, and 50 m from the conceptual well.

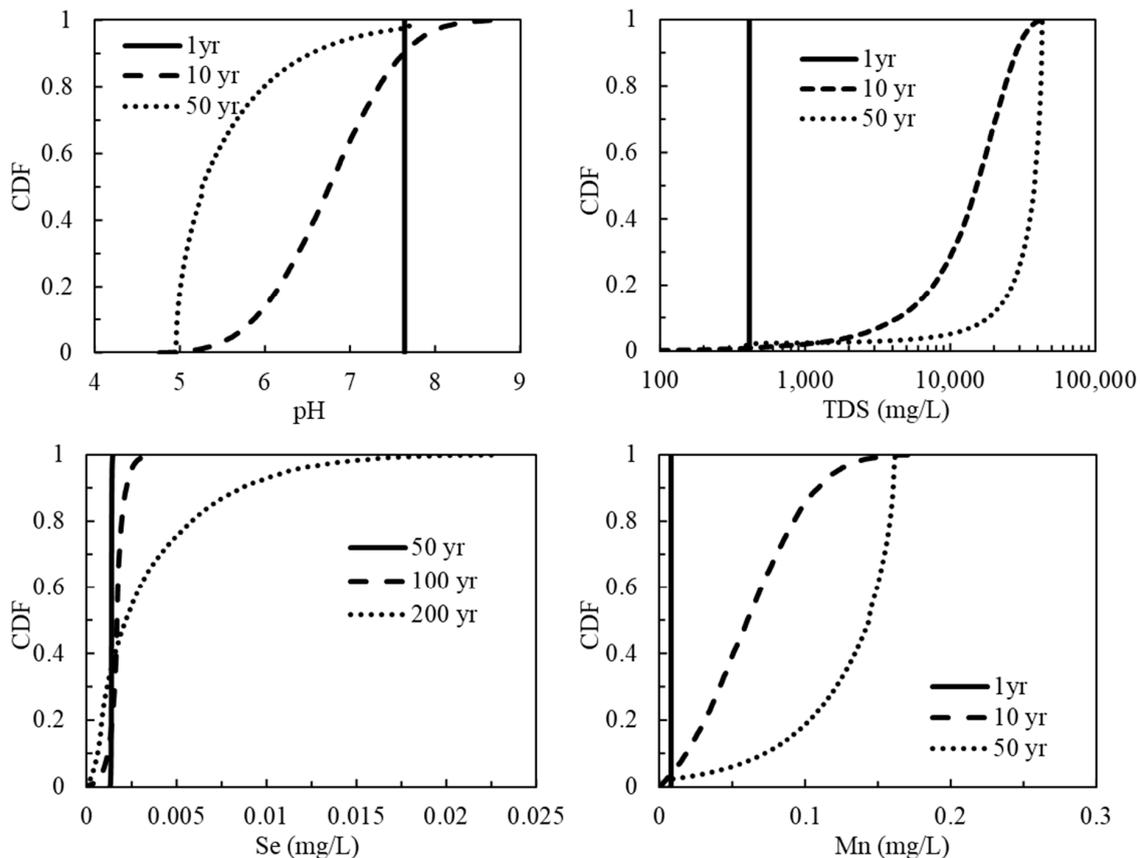


Figure 4. Cumulative distribution functions (CDFs) of pH, TDS, Mn and Se concentrations at 10 m from the conceptual well.

The CDF curves of pH, TDS, Mn and Se at 10 m away from the leaky well are shown in Figure 4. The RSM model results (10,000 random cases) suggest that the groundwater would not be largely impacted by the leakage within 1 year, but there are significant changes in pH, TDS, and Mn concentrations after 10 years. After 50 years, these concentrations maintain at a stable level (the curves beyond 50 years are not shown for pH, TDS, and Mn) because the gas saturation and dissolved CO₂ concentration reach a steady state at this location. However, the response of Se concentration would not start until 100 years after the leakage starts, due to adsorption onto the sediment. For As, it does not show any significant changes even near the well, because its concentration in the leaked brine is not significantly higher than that in the groundwater. It indicates that clay minerals could mitigate trace metal mobilization within a certain extent with surface complexation reactions of the Ogallala aquifer, which is beneficial for the aquifer maintaining its quality. To the contrary, the high salinity and the metals not reactive

with sorbents (clays) of the leaked brine may likely be a larger concern in this case (TDS and Mn). Similar results are also obtained by other studies [17,63].

Overall, the leakage plume would reach ~50 m away from the well within 200 years of leakage from the reservoir with 0.4% injection rate in maximum. In the area impacted by the plume of radius 50 m from the well, pH, and TDS illustrate significant changes, because of the introduced acid plume with high salinity and reactivity with the sediment. Adsorption of trace metals onto clay minerals would hinder their mobilization within 200 years, which may reduce the risks of trace metal contaminations. Usually shallow groundwater monitoring wells are located farther than 50 m apart from each other, thus it might be difficult to detect water chemistry changes within a short time after leakage occur.

3.2. Thresholds and Indicators for Early Detection Criteria

The principles to choose indicators for early detection include: (1) easy to test, and (2) with significant changes due to a leakage, compared to the selected threshold. Usually groundwater chemistry varies over time due to groundwater flow and weather, and it might be difficult to indicate a leakage if the change is insignificant. Therefore, it is important to select a reasonable threshold for the indicators as well as indicators sensitive to potential leakage.

The probabilities of water chemistry occurrence ranges are used to forecast the likelihood whether the groundwater quality would be impacted by potential CO₂ and brine leakage with changes of water constituent concentrations. Figure 5 illustrates the probability of pH exceeding the state and federal MCLs and the site-specific no-impact threshold at different distances from the conceptual leaky well.

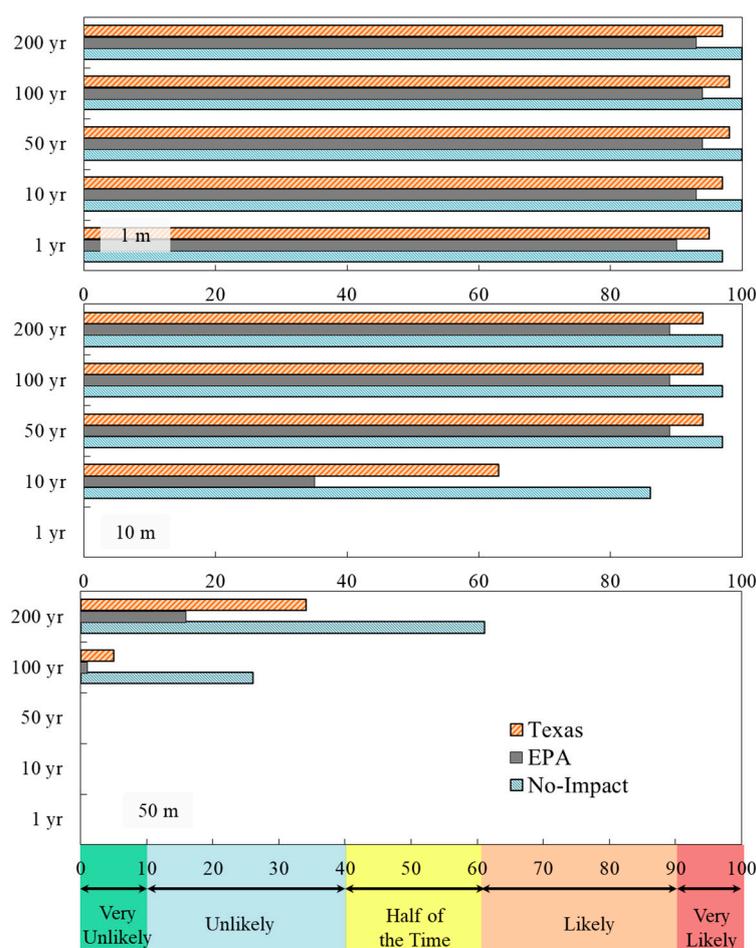


Figure 5. Probability of occurrence for pH exceeding the Texas MCL, the EPA MCL and no-impact threshold at 1 m, 10 m, and 50 m away from the leaky well.

At the distance 1 m away from the well, with large impacts of the leakage plume, a high probability for pH suggests that it is likely to exceed all three thresholds (> 95% probability) with limited differences, because significant pH drops (< 6.0) occur due to the leakage. At the distance 10 m away from the well, it is very unlikely to identify any pH change in the first year since the acid plume does not reach this distance. After 10 years, it is likely to determine the pH change using no-impact threshold compared to the MCLs. It starts to suggest pH changes exceeding the thresholds with a significant difference after 100 years at 50 m away from the well. It suggests that the no-impact threshold is more sensitive to indicate a leakage, because it is stricter than the MCLs. It indicates that no-impact thresholds associated with site-specific monitoring data could be a valuable reference for evaluation of leakage impacts, which is meaningful for quantifying water quality change, especially for those water parameters that are significantly different from the MCLs. However, with limited impact area (< 50 m) of the potential leakage plume, it might be difficult to detect any changes of water chemistry at a monitoring well, which is usually a few hundred meters away from each other.

Easy-tested water parameters that are sensitive to the leakage should be selected as early detect criteria. Figure 6 shows the likelihood of changes of the five parameters of interest at different distances from the well. Due to adsorption of trace metals, such as Se and As, their concentrations maintain at a low level and are not likely to exceed the thresholds for a long time (also shown in Figure 4). Thus, such trace metals may not be capable to be selected as indicators for leakage at early stages. pH and TDS are the most sensitive constituents to indicate a leakage among all the cases with various leakage rates. Particularly, it is one of the most convenient methods to test pH of a water sample. Therefore, pH could be selected as an early detection indicator at the FWU site.

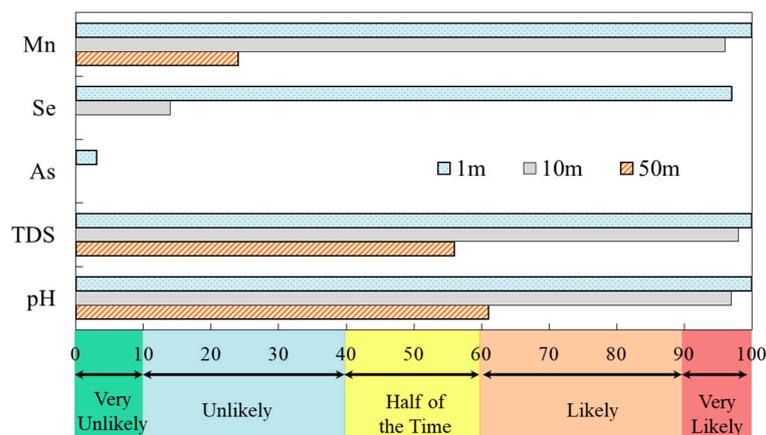


Figure 6. Probability of occurrence of pH, TDS, As, Se, and Mn exceeding the no-impact threshold at 1, 10, and 50 m away from the leaky well after 200 years.

4. Conclusions

In this study, we present a series of quantitative assessments of potential risks to the Ogallala aquifer with potential CO₂ and brine leakage at the FWU. Potential chemical risks to the overlying USDW aquifer were analyzed, and selected water constituents were evaluated for selecting early detection indicators. Salient findings include: (1) with leakage flux up to 0.4% of injected CO₂ and brine from a conceptual leaky well with failure, it is likely that the impacted area limits within 50 m from the well after 200 years; (2) toxic trace metals may be considered an insignificant long-term concern because of clay adsorption; (3) site-specific no-impact thresholds could be a preferable reference for groundwater quality evaluations; and (4) pH is suggested as a likely geochemical indicator for early detection of a leakage, due to its easy tested and sensitivity aspects. Results of this study provide a useful perspective of combining numerical simulations, field observations, and quantitative ROMs for site-specific risk assessment.

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