Development of Framework for a Groundwater Monitoring Program at a Geological Carbon Sequestration/Enhanced Oil Recovery Site

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Introduction
Carbon dioxide capture and sequestration in deep geological formation is increasingly being viewed as an important strategy for reducing greenhouse gas emissions (IPCC, 2007). Depleted oil and gas fields could serve as reservoirs for carbon sequestration under appropriate conditions (Benson and Cole, 2008). The injection of carbon dioxide into these reservoirs could be useful to displace oil and gas that is tightly held under residual saturation conditions and provide a financial incentive for carbon sequestration. Using carbon dioxide for enhanced oil recovery (EOR) has been practiced for over 40 years in the US (Duncan et al., 2009). It is estimated that nearly 50 million metric tons of CO$_2$ are used in the US for EOR with about 25% (12 million metric tons) coming from carbon dioxide of anthropogenic origin (Plasynski and Damiani, 2008). Currently, CO$_2$ is used in 37% of all EOR operations in the US. With maturing oil fields and a greater interest in reducing carbon dioxide emissions, this technology is likely to be used to a far greater extent in the future. CO$_2$ capture is becoming necessary at many coal fired power plants to meet federal regulations (Horazak et al., 2014) and EOR, it appears, provides an economically viable outlet for its reuse (Damiani et al., 2012).

While carbon dioxide based enhanced oil recovery has been practiced for over four decades, there are significant operational risks associated with capturing, compressing, transporting and injecting (and potentially sequestering) CO$_2$ (Duncan et al., 2009). In particular, mature oil fields could contain improperly plugged boreholes and wells, and properly placed plugs that may have deteriorated over time as well as abandoned wells and uncharacterized faults. The risk of migration of carbon dioxide, other deeper reservoir fluids (e.g., brine, petroleum hydrocarbons, methane) from these natural and artificial penetrations and the potential contamination of surficial groundwater resources is often cited as the primary risk factor when implementing carbon sequestration and/or carbon dioxide based
enhanced oil recovery (e.g., Gasda et al., 2004, Nordbotten et al., 2004, Wilson et al., 2007, Tsang et al., 2008, Benson and Cole, 2008, Sharma et al., 2009, Price and Oldenburg, 2009, Oldenburg et al., 2009; Oldenburg et al., 2011, Vilarrasa et al., 2013; Zahasky and Benson, 2014).

Carbon dioxide leakage diminishes the benefits of sequestration and must be properly accounted for to ensure emission reduction credits and benefits are properly allocated. Therefore, the utility of pressure monitoring wells (Nogues et al., 2011) and evaluation of fiber-optic sensors to measure carbon dioxide has also been studied (Orghici et al., 2008, Delgado-Alonso and Lieberman, 2013, Yang et al., 2014). Carbon dioxide is highly soluble in water and can trigger a variety of geochemical reactions when CO$_2$ escapes from the deeper formations and mixes with groundwater in shallower aquifers (Stumm and Morgan, 1995). Laboratory, field and modeling studies have been completed to identify likely changes in water quality when carbon dioxide gets added to aquifer formations (Humez et al., 2014; Trautz et al., 2012; Yang et al., 2012; Yang et al., 2013; Yang et al., 2014; Romanak et al., 2012; Van Pham et al., 2012; Hovorka et al., 2011; Kharaka et al., 2010; Wilkin and DiGuilio, 2010; Little and Jackson, 2010; Lu et al., 2010; Smyth et al., 2009; Kharaka et al., 2009; Norton et al., 2009).

While studies focused on developing new and innovative monitoring instruments and identifying potential geochemical interactions provide valuable insights regarding the parameters that need to be monitored and potential ways of observing them effectively at a high resolution, it is also important to establish a groundwater monitoring program (groundwater monitoring well network, schedules of measured water quality parameters and analytes, and protocols for conducting monitoring activities) that will enable early detection of fluid intrusions from deeper reservoirs as well as assess long-term changes that occur to groundwater resources over time and elucidate the likely role sequestration and enhanced oil recovery operations may have played in any identified change to groundwater resources. A well-designed monitoring program addresses basic questions such as – what to sample, when to sample and where to sample (Uddameri and Andruss, 2014a). Studies have focused on designing
monitoring networks for detection of groundwater contamination from waste disposal sites (Meyer et al., 1994; Storck et al., 1997; Mahar and Datta, 1997; Dhar and Datta, 2007), develop sampling plans to support groundwater remediation (Aziz et al., 2003, Nunes et al., 2004, Reed and Minsker, 2004) and evaluate regional water availability and water quality trends (Hudak et al., 1995; Reed et al., 2000; Zhang et al., 2005; Yeh et al., 2006; Mogheir et al., 2009; Daughney et al., 2012; Kollat et al., 2011; Uddameri and Andruss, 2014a; Uddameri and Andruss, 2014b; Esquivel et al., 2015). However, to the best of the authors’ knowledge, studies aimed at developing guidance on groundwater monitoring programs at carbon sequestration and reuse CO₂ based EOR sites have not been completed. The design of a monitoring program framework for monitoring groundwater resources near the proposed West Ranch CO₂-EOR site is the focus of this study.

Conceptual Model of CO₂-EOR Operations
Development of a monitoring program must be based on the sound understanding of the system that needs to be studied. A conceptual model of a CO₂-EOR operation is schematically depicted in Figure 1. Enhanced oil recovery (EOR) operations involve injecting fluids (CO₂ in this case) into a reservoir containing brine and oil. EOR is a secondary recovery operation used to extract oil from otherwise depleted reservoirs. As such, the oil is held in the pores under the influence of capillarity (under residual saturation conditions) with the majority of the pore space occupied by the brine. While several different configurations have been proposed, the five-spot injection-extraction pattern is commonly used in EOR operations (Rose et al., 1989) and adopted here. The injection of CO₂ occurs at the four outer wells and the inner well is used for the extraction of brine and oil. Based on the site conditions, there could be continuous injection of CO₂, alternating cycles of brine and CO₂ (water and gas or WAG) and simultaneous injection of water and CO₂ (SWAG) (Dai et al., 2013).
CO₂ is injected as a supercritical fluid into a reservoir containing brine and results in a two fluid phase system. The injected CO₂ seeks to displace the brine but being lighter than brine and more buoyant tends to move upward. After a certain period of time, the region around the injection well becomes mostly saturated with CO₂ but the carbon dioxide plume extends to a certain distance along the edge of the caprock (Nordbotten and Celia, 2006).
As depicted in Figure 2, the reservoir can be envisioned to contain – a dry region containing $CO_2$, a wet region containing brine, and an intermediate region containing a mixture of both. Prior to injection, the pores of the reservoir are saturated with brine. The additional mass forced into the reservoir by injecting $CO_2$ is accommodated by – 1) Dissolution of carbon dioxide into the brine; 2) increasing the fluid pressure, 3) displacement of brine (or $CO_2$) at the openings of the formation, if any and 4) uplift of land surface (Nicot et al., 2009). The zone of elevated pressure is of primary concern at many sites as it can extend over very large distances even when the $CO_2$ plume has only traveled a short distance away from the well. $CO_2$ plume in the reservoir and the pressure increases caused due to $CO_2$ injection are often viewed as the primary risk factors for contamination of shallow groundwater resources. Clearly, the highest risk is posed in the area surrounding the injection and extraction wells as well as those surrounding artificial and natural penetrations. Therefore, the monitoring program of surficial aquifers must be designed such that it identifies any contamination plumes arising from accidental releases of contaminants from deeper formations into the shallower aquifers.
Study Area
A project has been proposed to sequester approximately 1.6 million tonnes of CO$_2$ from the W. A. Parrish Coal-fired Power Plant in Fort Bend County, Texas. The project includes the transport of captured CO$_2$ for use in enhanced oil recovery (EOR) operations to the West Ranch Oilfield in Jackson County, Texas (Figure 3). The EOR project site has a footprint of approximately 5,500 acres. The enhanced oil recovery (EOR) efforts will be directed to the Frio formation that includes Greta, Glasscock, Ward, 41-A, 98-A Sand Units. The Frio Formation occurs approximately 5,000 feet below mean sea level (MSL) and is approximately 2,500 feet thick and is interchangeably referred to as the reservoir here. The Frio Formation is overlain by Anahuac Formation, which is approximately 1,600 feet thick in the southeastern part of Jackson County but progressively thins moving northwest (Eby, 1943). The Anahuac Formation has fairly low permeability (~ $5 \times 10^5$ mD) and is expected to serve as the caprock of the reservoir and is estimated to be about 1,000 feet thick beneath the West Ranch Oilfield (Hilcorp, 2015).
The Frio Formation, Anahuac Formation and Catahoula Tuff are collectively referred to as the Catahoula Confining System (Davidson and Mace, 2006). The Catahoula Confining System is overlain by the Jasper Aquifer of the Gulf Coast Aquifer System, which consists of the Oakville Sandstone and Fleming Formation. The Jasper Aquifer has also been defined to include the lower Lagarto Unit of early Miocene Age, the early Miocene Oakville Sandstone Member of the Fleming Group, and the sandy intervals of the Oligocene-age Catahoula Formation (Young et al., 2010). The upper part of the Fleming Formation forms the Burkeville Confining System of the Gulf Coast Aquifer System that separates the Jasper Aquifer from the Evangeline Aquifer, which is made up of water within the Goliad Sand Formation. The shallowest component of the Gulf Coast Aquifer System, the Chicot Aquifer, is made up of the Willis Sand, the Bentley and Montgomery Formations, the Beaumont Clay, and alluvial deposits at the surface (Baker, 1979; Davidson and Mace, 2006; Chowdhury and Turco, 2006). The stratigraphic description of the Gulf Coast Aquifer System as defined by the Texas Water Development Board Central Gulf Coast Groundwater Availability Model (Chowdhury et al., 2004) near the West Ranch and augmented with details of the Catahoula Confining System provided in NETL (2012) form the basis for the stratigraphic conceptualization shown in Figure 4.
The thicknesses of the four stratigraphic components of the Gulf Coast Aquifer System exhibit variability near the West Ranch site, which is depicted in Figure 5. The thicknesses of the components generally increase eastward. The Gulf Coast Aquifer System is generally comprised of inter-beded layers of sands, silt and clays. The Burkeville Confining Unit is primarily comprised of silts and clay, while the Evangeline Aquifer has a higher sand to clay ratio. The Chicot Aquifer is under unconfined conditions near the West Ranch while the Evangeline Aquifer, Burkeville Confining Unit and Jasper Aquifer are all under confined conditions. The Catahoula Formation is mainly comprised of pyroclastic and tuffaceous sandstones (Baker, 1979). The sediments of the Gulf Coast Aquifer System were deposited in fluvial-deltaic or shallow marine environments (Sellards, 1932). Repeated sea level transgressions and regressions as well as subsidence has led to cyclical and discontinuous sedimentary deposits of sand, silts and clays.
The mineralogy of the shallower sediments of the Gulf Coast Aquifer System has not been studied well (Chowdhury and Turco, 2006). The mineralogical composition of the sediments of the Catahoula Formation have been analyzed and are comprise of 20% - 80% quartz with the lower percentages in the south and progressively increasing northward. The quartz composition is generally inversely correlated with feldspars (Lindquist, 1977). The Goliad Formation (Evangeline Aquifer) is considered genetically and compositionally similar to sandstones of the Catahoula Formation but with greater amounts of caliche containing up to 30% calcium carbonate (Sellards, 1932). The clays are primarily comprised of montmorillonite but also contain trace amounts of illite, kaolinite and chlorite (Gabrysch and Bonnet, 1975).

![Diagram of Depths of Various Hydrostratigraphic Units](image)

*Figure 5: Depths of Various Hydrostratigraphic Units of the Gulf Coast Aquifer System near West Ranch Site, Jackson County, TX. (Data from Chowdhury et al., 2005. Note: the area here corresponds to the circular buffer depicted in Figure 1)*
EOR operations are proposed using multiple overlapping five-spot injection extraction patterns with each pattern covering 40 acres. It is estimated that 120 injection wells and 120 extraction wells will be utilized over the 20-year lifespan of the project (NETL, 2015). Hilcorp Energy, Inc has requested, and the Railroad Commission of Texas has granted, permits authorizing the injection of 20,000 barrels of water per well into the Frio Formation to achieve minimum miscible pressure in the reservoir prior to initiating CO₂ based EOR. At minimum miscible pressure no interfacial tension exists between the fluids and the crude oil will be miscible in CO₂.

Groundwater Monitoring Network Design
Defining Monitoring Objectives
The first step in the design of a groundwater-monitoring framework is to clearly define the goals and objectives for associated monitoring program. This is particularly important because groundwater monitoring often has to reconcile conflicting objectives (Reed and Minsker, 2004). Groundwater monitoring at a site can be carried out from multiple perspectives and the choices made for where to monitor and what to monitor certainly affected by that perspective. Operators at CO₂ based EOR sites and regulatory agencies charged with the oversight of these operations would likely be interested in a focused site-specific sampling effort in order to ensure the operations are carried out safely and are compliant with applicable standards. On the other hand, agencies entrusted with conservation and protection of regional water resources would likely seek to design and implement a monitoring program, including the installation of a monitoring network, that ensures groundwater resources at the site are protected and any deleterious effects to groundwater quality caused by operations at the site are immediately contained and the effects do not impact water availability or quality of neighboring landowners. As monitoring is expensive and successful groundwater monitoring often hinges on obtaining access to wells on privately owned lands, it is important that monitoring objectives be transparent and be guided by stakeholder inputs (Uddameri and Andruss, 2014b). Inclusion of
stakeholders is not only critical to accomplish groundwater monitoring but also for the overall success of carbon capture and storage projects (Wilson et al., 2007).

The goals and objectives for the framework designed by this study are derived from the mission of the Texana Groundwater Conservation District has established in the Management Plan of the District, Chapter 8857 of the Special District Local Laws Code, and Chapter 36 of the Texas Water Code, which tasks the District with conserving and protecting groundwater resources within Jackson County. Therefore, the primary objective of the proposed framework is to enable the immediate detection and characterization of any contamination to groundwater resources due to sequestration and enhanced oil recovery operations at the site as well as ensure that any potential contamination or harmful alterations to water quality are localized and do not affect surrounding areas.

Defining Monitoring Area
Delineation of appropriate monitoring area is an important component in the development of a groundwater-monitoring framework at carbon sequestration sites. In most groundwater monitoring applications, the area to be monitored is known a priori and based on natural or administrative boundaries (in case of regional networks) or based on existing groundwater contaminant plumes in remediation applications. The United States Environmental Protection Agency (USEPA) has defined the Area of Review (AoR) as the area surrounding the geological sequestration project where underground sources of drinking water (USDW) may be endangered by injection activity (USEPA, 2013). For most types of injection wells, AoR are generally defined as a fixed radius (1/4 mile of Class II enhanced oil recovery wells and 2 miles for Class I hazardous waste wells). Injection wells used for geological carbon sequestration are classified as Class VI wells and the final rules for federal requirements associated with class VI wells were published by USEPA in 2010. USEPA (2013) recommends an advanced AoR for Class VI wells wherein the area likely to experience pressure buildup due to injection is defined as AoR. Mathematical models are recommended for defining AoR for Class VI injection wells. Nicot et al., (2011)
demonstrate that with suitable modifications, simpler single-phase simulation models can mimic the behavior of compositional simulators particularly at far-field conditions and used for delineating AoRs. Federal regulations require owners and operators of injection wells to identify all potential conduits within the AoR including artificial penetrations (open bore holes) and perform necessary corrective actions to prevent fluid movement into a USDW. Fluid movement into aquifers not used for drinking water purposes are not regulated by federal Underground Injection Control (UIC) statutes. When carbon dioxide is injected underground for the purposes of enhanced recovery (ER), the injection wells can continue to be permitted as Class II wells, regardless of the source of CO₂ (Grevatt, 2015). While all Class VI wells are directly regulated by USEPA, many states have primacy over Class II injection wells. As such, the AoR at the West Ranch site would be of ¼ mile radius and is insufficient to meet the far-field groundwater monitoring objectives.

A five-mile radius buffer was delineated around the proposed site (as shown in Figure 3) and is taken as the region of interest for the purposes of groundwater monitoring. As stated previously, Railroad Commission of Texas requires an area of review of ¼ mile radius surrounding the injection of Class-II injection wells. However, Nicot et al., (2009) indicate that the pressure perturbations associated with large-scale CO₂ injection can extend several kilometers from the injection site and further than the actual CO₂ plume itself. Delineating an area to be monitored that is small and local to the injection wells will not enable the detection or characterization of impacts associated with far-field pressure perturbations, if any. On the other hand, delineating a monitoring area that is too large will likely decrease the chances of detecting near-site excursions due to the limited groundwater monitoring resources being widely distributed. Therefore, the proposed five-mile radius region of interest for this framework represents a balance between identifying and characterizing local (injection-site) impact and the regional (far-field) impacts. The area within this five-mile region of interest includes the 1,600 acre West Ranch Field and is referred to as monitoring area of interest (MAI) in this study.
What to Monitor
Accidental releases from CO2-EOR sites can release several different kinds of chemicals into the environment. For planning purposes, these chemicals can be classified as – 1) those arising from accidental releases of carbon dioxide into aquifers and 2) those arising from accidental release of brines and produced water into aquifers. Therefore, analytical monitoring at CO2-EOR sites must include monitoring of both inorganic and organic constituents as carbon dioxide incursions in a shallow aquifer affect the inorganic chemical constituents brought forth by water-mineral interaction facilitated by pH alterations and accidental releases of produced water affect the inorganic chemistry (cations, anions from brines) as well as organic constituents from petroleum hydrocarbons.

The addition of even small amounts of carbon dioxide is shown to cause immediate changes in pH (Little and Jackson, 2010), which has been confirmed in several field and laboratory experiments. Inorganic carbon measures include dissolved inorganic carbon (DIC). Bicarbonate and carbonate concentrations are also noted to increase in field and laboratory studies and as such provide another set of chemical-specific constituents useful in early detection of carbon dioxide leakage into shallow aquifers (Wilkin and DiGuilio, 2010). The decrease in pH is accompanied by an increased alkalinity and as such total alkalinity is another useful measure to detect changes in aquifer quality (Norton et al., 2009). Alkalinity is also known to be better indicator than pH in aquifers containing minerals such as calcite, which tend to buffer pH (Wilkin and DiGuilio, 2010). Total dissolved solids (TDS) and specific conductance (EC) are two other bulk indicators that are likely to increase when CO2 is added to aquifer waters as decrease of pH can lead to dissolution of feldspar and carbonates (Lu et al., 2010; Kharaka et al., 2010). Monitoring of TDS and EC is advantageous from the standpoint that they are easy to measure in the field and can be monitored continuously with rather inexpensive instrumentation. Elevated levels of TDS are indicative of mixing between waters of the deeper reservoirs and shallow groundwater.
The concentration of inorganic chemicals also changes when carbon dioxide is added to water. In a field study conducted in Bozeman, MT, Kharaka et al., (2010) found that concentrations of Ca, Mg, Fe and Mn increased upon CO\textsubscript{2} injection while Na concentrations were relatively stable. The concentrations of trace metals such as Pb, As, Zn also exhibited increasing trends but these increases were difficult to confirm as the concentrations are close to detection limits. Trautz et al., (2012) found that Ba, Ca, Cr, Sr, Mg, Mn, Fe exhibited a pulse behavior (an increase followed by a decrease in concentrations) while As and Pb were below detection limit at a controlled field experiment site in Mississippi. In a laboratory study, Lu et al., (2010) found that Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, Zn rapidly increased following initial CO\textsubscript{2} flux and reached stable concentrations before the end of the experiment. Type II cations (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) increased at the start of CO\textsubscript{2} flux, but declined, in most cases, to levels lower than pre-CO\textsubscript{2} concentrations. In a laboratory study with different aquifer sediments, Little and Jackson (2010) found that the concentrations of alkali and alkaline earth metals Li, Mg, Ca, Rb, Sr as well as those of some transitional metals Mn, Fe, Co, Ni, and Zn increased across all sediments. However, concentrations of Cd, Co, Al, V, As, Se, and Sb exhibited sediment specific behavior (i.e., increased in some and decreased in other sediments).

The behavior exhibited by metals and trace elements are dictated by the nature and extent of chemical reactions that take place in the subsurface environment. The presence of carbonate minerals (e.g., calcite and dolomite) tends to buffer the acidity and cause a smaller reduction in pH (Lu et al., 2010). Elevated carbon dioxide concentrations can induce reactions with silicates to produce bicarbonate (HCO\textsubscript{3}\textsuperscript{-}). However, these reactions proceed at a slower rate and are dominant when there are no carbonate minerals in the aquifer (Norton et al., 2009). Reactions with silicates at a certain distance from the injection site can cause increases in pH and re-precipitation of carbonate minerals and this phenomenon has been observed in the Frio formation in the Texas Gulf Coast (Kharaka et al., 2006). In addition, carbon dioxide can also interact with oxyhydroxides (Geothite, hematite) and sheet silicates.
(smectite and illite), which can release cations and buffer pH. Wang and Jaffe (2004) illustrate that elevated levels of carbon dioxide in water can cause dissolution of lead (Pb) from Galena. Elevated levels of bicarbonate are known to increase the mobility of arsenic (As) in groundwater systems by desorbing arsenic absorbed to iron oxyhydroxides (Anawar et al., 2004). The behavior of inorganic compounds noted in carbon dioxide injection experiments depends upon the quantity of inorganics present in the mineral matrix as well as the ambient water quality of the aquifer. Pulsed or short-term increases followed by subsequent decreases are often hypothesized to be due to fast desorption and/or surface dissolution reactions where the availability of the constituent is low.

Given the findings in the literature, it is recommended that inorganic chemicals including major cations and anions (Ca, Mg, Na, K, Cl, HCO\(_3\), CO\(_3\), and SO\(_4\)) be monitored periodically at the site. Furthermore, it is recommended that the monitoring program also include sampling of trace elements - Mn, Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni, Cu, Co, Al, V, Se, and Sb as these compounds provide vital clues with regards to carbonate and silicate reactions in the aquifer induced by carbon dioxide incursions. As concentrations of many chemical constituents and their mobility (or lack thereof) depend upon the aquifer mineralogy, it is also recommended that detailed characterization of aquifer solids be carried out at the site. Solid phase characterization can be carried out using either structural or functional approaches (USEPA, 1998). In the structural approach, the elemental composition of the aquifer minerals are directly measured using techniques such as X-Ray Diffraction spectroscopy (XRD), Atomic Force Microscopy (AFM), Raman Spectroscopy. In the functional approach, the sediments are made to come in contact with water and the amount of chemical that is released as well as rate of dissolution, precipitation and/or uptake is estimated using sequential extractions (Tessier et al., 1979; Yanase et al., 1991). It is strongly recommended that aquifer sediments be characterized using one of the two approaches. However, the structural approach while direct requires costly instruments and multiple micro-scale
samples and may be difficult to conduct when the samples are close to the detection limits of the instrumentation (USEPA, 1998).

Contamination from produced water injected to manage formation pressures is another possibility at CO₂-EOR sites. Produced water is the water that co-extracted during oil and gas production. Approximately 3 – 10 barrels of produced water is extracted for each barrel of hydrocarbons during oil and gas operations (Khatib and Verbeek, 2003; Veil et al., 2004). Produced water contains dissolved and dispersed organic compounds including but not limited to benzene (B), toluene (T), ethylbenzene (E) and xylenes (X), polyaromatic hydrocarbons (PAH) such as naphthalene. The aqueous solubility of many petroleum hydrocarbons is extremely low. Therefore, the presence of a dispersed oil phase is also to be expected. Total oil and grease is a bulk measurement commonly used to evaluate the presence of dispersed oil and gas. In addition, total petroleum hydrocarbons (TPH) C3 – C12 compounds, diesel range organics (DRO), (C9-C21) carbon compounds, kerosene (C8 – C15), BTEX compounds, and phenols are most soluble of organic compounds and are classified as known or suspected carcinogens and provide good indicators of potential contamination. BTEX compounds are also highly degradable in aquifers and BTEX plumes generally extend approximately 150 – 200 feet from the source (Newell and Connor, 1998).

The salinity of produced water can be significant (> 100,000 mg/L) and mainly reflects the connate water from the reservoir from which oil and gas is produced. The connate waters are likely to be enriched in sodium (Na) and chloride (Cl) compared to other major cations (i.e., Ca, Mg, K) and anions (HCO₃). Elevated levels of sulfate (SO₄) is also noted in produced water and as such can serve as a good indicator to monitor for contamination from produced waters (Duckworth, 2011). Trace metals such as cadmium (Cd), chromium (Cr), copper (Cu), zinc(Zn) can be found in relatively higher levels in produced waters (Hansen et al., 1994) compared to their typical concentrations in shallower aquifers. Naturally
occurring radionuclides (NORMs) are another important class of compounds that are often associated with oil and gas production (USGS, 1999). The solubility of radium increases due to presence of chloride and elevated levels of radium, uranium and radon may also serve as useful indicators for contamination of aquifers due to produced water leakage. Several ionic and polar organic compounds are used during the production of oil and gas to prevent corrosion, inhibit scale formation, break up foams (anti-foaming agents) and prevent microbial growth (biocides). While the quantities of these compounds are often used in trace quantities, some of the chemicals such as the linear alkylbenzene sulfonate (LAS) are soluble in water and provide evidence of leakage. Generally, the products used during oil and gas operations are proprietary and protected as trade secrets and as such their exact composition may not be completely known.

Tracers are compounds injected into oil reservoirs to evaluate potential leakage. Freon has been employed as a tracer in CO2 based enhanced oil recovery (Craig III, 1985). Perfluorocarbon tracers (PFTs) such as perfluoro-1,2-dimethylcyclohexane (PDCH), perfluorotrimethylcyclohexane (PTCH) and perfluorodimethylcyclobutane (PDCB) have also been used to detect leakage (Ljosland et al., 1993; Freifeld et al., 2005; Wells et al., 2007). Wells et al., (2007) injected small quantities (500 mL) of PDCH, PTCH and PDCB along with 12 tons of CO2 at a depleted oil reservoir in Southern New Mexico. The tracers were monitored in soil has around the injection wells. Tracers were detected in subsurface soil gas within days of injection and continued to be detected in a radial pattern for 100 m and up to 300 m in some directions. PFT tracers are widely used in environmental and atmospheric applications and have the potential to detect CO2 leakages. Myers et al., (2013) provide a detailed review of the use of tracers in CO2 sequestration projects. They recommend the use of PFTs as they are widely available, have low analytical detection limits and are environmentally stable. However, the sampling of soil gas must be carefully done by placing an absorbant (ambersorb) into a capillary absorbant tube system (CATS). Atmospheric sampling using gas-tight syringes has also been tested by Wells et al., (2007). Soil
gas sampling must avoid potential interferences caused by roots, rainfall percolation and other preferential flowpaths (e.g., worm holes) to obtain representative samples, CATS must be placed 1 – 3 m below the ground surface. Perdeuterated CH₄ (CD₄) has also been used as a tracer as its properties are much closer to CO₂ then many common PFCs (Boreham et al., 2011). However, CD₄ can undergo microbial degradation, which may limit its utility for long-term monitoring (Madsen, 2011).

Naturally occurring isotopes offer another mechanism for detection of leakages at CO₂-EOR sites. The isotopic composition (¹²C/¹³C) of injected CO₂ is known to be different from the naturally occurring CO₂ and has been used to identify the CO₂ plume associated with carbon sequestration (Johnson et al., 2011). The δ¹³C ratios in shallow groundwater and deeper reservoir could provide an indication of mixing of deeper reservoir brines with shallower groundwater. Deeper brines generally have not been exposed to the surface after the 1950s should contain trace or no tritium $^3$H while freshly recharged waters in the shallower aquifers will contain higher concentrations of tritium created by nuclear testing. Thus, decreases in tritium concentrations could serve as another useful indicator to identify leakage of brines. The ratio of methane/ethane is generally between 1 – 100 if these compounds are of thermogenic (deeper) origin and are in the 1000 – 100000 range when methane is of biogenic origin. In addition, δ¹³C-CH₄ and δ²H-CH₄ isotopic compositions vary substantially between methane present in shallower formations and those from deeper formation (thermogenic origin) (Osborn et al., 2011).

The introduction of CO₂ into shallow aquifers (due to potential leakage) will affect the microbial processes that are operative in the subsurface. These microbial processes define the redox conditions in the aquifer and as such affect the mobility of metals and degradation potential of organic compounds in the shallower aquifers. CO₂ is often used as a bactericide in the food industry and CO₂ can penetrate the cell walls of microorganisms and affect their metabolism (Schultz et al., 2012). Wu et al., (2010) studied
the effects of CO₂ stresses on Shewanella oneidensis MR-1 an environmentally relevant and commonly found strain of bacteria. Their experiments indicate while MR-1 is capable of recovering from short-term CO₂ exposures, the decrease in pH and sustained high pressure CO₂ exposure causes permanent damage to cell walls. CO₂ additions can however be beneficial to lithoautotrophic bacteria in the presence of electron donors such as H₂, Fe²⁺, Mn²⁺ if the concentrations of CO₂ are below toxic levels (Lions et al., 2014). Microbial community structures will likely change when CO₂ is introduced into the aquifer and may provide another mechanism for CO₂ leak detection. However, its use is likely impractical as baseline microbial communities must be properly established and sampling and monitoring of microbial characteristics is expensive as well (Noble et al., 2012).

Table 1 presents a list of chemicals that can be potentially monitored at CO₂-EOR sites and was developed based on the literature review presented above. The sampling costs are only provided as an initial approximation and can vary widely depending upon the Quality Assurance/Quality Control (QA/QC) protocols selected as well as the nature of instrumentation to be used. Many common constituents can be analyzed relatively cheaply using standard kits (Hach, Inc.) while such analysis are useful for screening purposes, they are not suitable for regulatory compliance monitoring. In a similar manner, hand-held photoionization detectors can be used for screening hydrocarbon contamination quickly and inexpensively but again are only useful for screening purposes. The use of screening methods to augment regulatory compliance sampling and monitoring certainly makes sense. It is also important to remember that proper protocols for sample collection, preservation and shipment must be adhered to in order to increase the integrity of the data and these entail costs as well.

Table 1: Analytes of Interest at CO₂-EOR Sites
<table>
<thead>
<tr>
<th>Chemical Class</th>
<th>Chemical Constituents</th>
<th>Recommended Frequency Schedule</th>
<th>Approximate Costs/Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Constituents</td>
<td>TDS, Specific Conductance, total Hardness, ORP</td>
<td>Continuous or high frequency</td>
<td>$3000 - $5000 per field probe</td>
</tr>
<tr>
<td>Major Ions</td>
<td>Ca, Mg, Na, K, CO₃₂⁻, SO₄²⁻, HCO₃⁻, Cl</td>
<td>Quarterly (Na and Cl could be monthly initially)</td>
<td>$100 – 200 per well</td>
</tr>
<tr>
<td>Trace Constituents</td>
<td>Cd, Cr, Cu, Zn, As, Ba, Sr, Mn, Ni, Cs, Fe, U, V, Mo, Al, PO₄³⁻, NO₃⁻, NO₂</td>
<td>Quarterly or semi-annually. Higher frequency when excursion is noted</td>
<td>$50 - $500 depending upon the number and type</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Oil and Grease, Total Petroleum Hydrocarbons (TPH), Diesel Range Organics (DRO), Benzene, Toluene, Ethylbenzene, Xylenes</td>
<td>Quarterly</td>
<td>$50 - $100 per sample</td>
</tr>
<tr>
<td>Radioactivity</td>
<td>Gross Alpha and Gross Beta particles</td>
<td>Quarterly</td>
<td>$25 - $100 per sample</td>
</tr>
<tr>
<td>Environmental Tracers</td>
<td>perfluoro-1,2-dimethylcyclohexane (PDCH), perfluorotrimethylcyclohexane (PTCH), perfluorodimethylcyclobutane (PDCB)</td>
<td>Weekly - Quarterly</td>
<td>~ $500. Limited locations for analysis. Will also need set up to capture samples</td>
</tr>
<tr>
<td>Isotopes</td>
<td>¹²C, ¹³C, δ¹³C-CH₄ and δ²H-CH₄</td>
<td>Quarterly – Semi-Annual</td>
<td>~ $500 Limited locations for analysis.</td>
</tr>
</tbody>
</table>

In addition to water quality monitoring, performing aquifer sediment characterization prior to the beginning of operations at the site would yield useful information to understand any observed water quality changes after the operations have begun at the sites. As discussed previously aquifer sediment characterization is useful to identify mineral structure and understand chemical reactivity of the aquifer. Aquifer sediment characterization can be repeated once every few years especially if significant water quality alterations are noted at the site. Aquifer sediment characterization must certainly be a long-term monitoring goal if it cannot be performed before the start of sequestration and oil recovery operations.
Useful Water Quality Information that is Currently Unavailable
There are other water quality parameters that could potentially be used to detect brine, CO₂ and hydrocarbon leaks whose data are currently unavailable either within the MAI or in the county. These parameters include methane, oil and grease, total petroleum hydrocarbons (TPH), Diesel range organics (DRO), isotopic data as well as tracers such as perfluoroethenes (PFEs). The concentrations for many of these constituents are expected to be below detection limits (under pristine conditions). However, routine monitoring of these constituents can be helpful in identifying leaks and other accidental releases arising from both CO₂ sequestration and enhanced oil recovery (EOR) operations at the site.

Frequency of Sampling
The frequency of sampling must be established such that a monitoring objective (e.g., detection of an abrupt change, a monotonic trend) can be evaluated reliably. Reliable evaluation implies that the monitoring objective can be evaluated in a statistically relevant manner. Traditionally, parametric statistical tests used to minimize the risks associated with incorrectly rejecting the null hypothesis (referred to as the Type-I error). However, the risk of not rejecting the null hypothesis when in fact it is true is also of concern and referred to as the Type-II error. Type-II error decreases with the number of samples collected and as such has been used to identify frequency of sampling (Uddameri and Andruss, 2014a; Uddameri and Andruss, 2014b) and can be adopted here as well.

Statistical power analysis identifies the number of independent samples required to statistically assess monitoring objectives. Samples collected closely in time however exhibit significant autocorrelation, and the assumption of independence is not proper in this context. Redundancy may however be important when the goal is to detect water quality excursions in an expedient manner. The redundancy of data points can be corrected by computing an effective sample size (ESS). ESS is a measure of the number of independent data points present in an autocorrelated time-series. The ESS can be computed using the formula presented by Bayley and Hammersley (1946), which is given in equation 1. This
approach has been used by several researchers to reduce autocorrelation effects in hydrologic time series (Lettlemaier, 1976; Hamed and Rao, 1998; Yue and Wang, 2004; Uddameri, 2010).

\[
ESS = \frac{n}{1 + 2 \sum_{k=1}^{n-1} \left(1 - \frac{k}{n}\right) \rho_k}
\]  

(1)

Where, \(n\) is the number of total data samples, \(\rho_k\) is the \(k\)th lag autocorrelation coefficient and \(ESS\) is the effective sample size. The effective sample size can be used to correct for autocorrelation effects when performing statistical tests.

**Evaluation of Existing Groundwater Data near the West Ranch Site**

The primary goal of the groundwater monitoring program development is to apply it to guide sampling and monitoring activities at the West Ranch CO₂ – EOR site. The design of any monitoring program must make the best use of available data. An assessment of existing data helps one identify critical data gaps and also provides initial estimates of geochemical variability and help guide future monitoring activities. As such, a comprehensive evaluation of existing data at the West Ranch site was carried out and discussed below.

**Inventory of Groundwater and Oil and Gas Wells in the MAI**

The Texas Water Development Board (TWDB) groundwater database is the primary source of historical water well data in the vicinity of the site. The recent database (TWDB Database) was downloaded in November 2015 and queried to obtain data on historical water levels and water quality. The well depth information was matched with stratigraphy information obtained from Chowdhury et al., (2004) to identify the aquifers in which various wells were located. A total of 90 wells were identified within the 5-mile buffer and are depicted in Figure 3. As can be seen, these wells do not follow any specific patterns and were mostly developed for the purposes of extracting water from the aquifers. Of the 90 wells, 64 are completed in the Chicot formation, 24 are completed in the Evangeline formation, and 2
are deep wells completed in the Catahoula Formation. While the Chicot formation is 600 – 800 feet below the land surface, most existing water wells are shallow with the deeper Chicot Aquifer wells extending to only 400 – 500 feet below ground surface. The existing wells completed in the Evangeline Aquifer are drilled to approximately 900 – 1400 feet below ground surface even though the aquifer itself extends over 2000 feet below ground surface. There were no wells within the TWDB Database identified as being completed in the Burkeville Confining Layer or the Jasper Aquifer. While there are no direct wells tapping in the Jasper Aquifer, the concentrations of dissolved solids in this aquifer are estimated to be over 10,000 mg/L total dissolved solids (TDS) based on information provided in Waterstone, (2003).

It is important to note that while 90 water wells can be identified from TWDB database as being located in the MAI (5-mile radius of the site), the database does not necessarily contain historical water quality data or vital construction information related to these water wells. Furthermore, the actual location of the wells may not be within the MAI as the accuracy of the positional data for a water well may be insufficient. Nonetheless, these wells provide an initial set of candidate wells for developing monitoring network at the site. A complete and accurate inventory of water wells including the precise locations, screening intervals, total depths, and baseline water levels and water quality measurement is vital to implementing a water quality monitoring program within the MAI.

An inventory of oil and gas wells was queried from the Texas Railroad Commission Database in November 2015. The 206 oil and gas wells depicted in Figure 3 include 25 that are currently active, 87 plugged, 34 temporarily abandoned. The depiction also contains a few wells that have been listed as drilled but not yet completed and 1 well that has been permitted but not yet drilled. A total of 154 of the 201 wells are localized within the West Ranch and tap into various oil bearing formations. Casing
(and other material) failures in existing and abandoned oil and gas wells provide connectivity between the deeper (oil bearing strata) and the shallower (water bearing strata) and the potential to bring brine, carbon dioxide and oil in contact with shallower (fresh) groundwater. Leakage of CO$_2$, brine and other fluids from abandoned wells due to structural defects and cement deterioration is well documented in the literature (Nordbotten et al., 2005; Benson and Cole, 2008; Kutchko et al., 2007; Nogues et al., 2011; Scherer et al., 2015).

**Groundwater Level Data and Groundwater Flow Delineation**

Monitoring of groundwater levels is necessary to calculate potentiometric heads, hydraulic gradients and delineate regional groundwater flow directions. Unless the injection and extraction operations at the site alter the groundwater flow paths locally, the migration of chemical plumes will be influenced to a certain degree by the regional groundwater flow. Recent groundwater level measurements were queried from the TWDB Database to delineate regional groundwater flow directions. Water level measurements are generally made annually at about 15 wells within Jackson County, TX. However, of these, only 2 wells are within the MAI. As such, site-specific hydraulic gradients could not be estimated and only the larger regional (county-wide) regional gradient could be ascertained from the data. The hydraulic gradient calculations were carried out using regression approaches (Devlin, 2003; Uddameri et al., 2014a) and summarized in Table 2.

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>West-East Gradient (X-Axis)</th>
<th>South-North Gradient (Y-Axis)</th>
<th>Regional Gradient</th>
<th>Angle</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chicot</td>
<td>-0.00021</td>
<td>0.000314</td>
<td>0.000375</td>
<td>-56.7878</td>
<td>Based on 13 well measurements in 2014</td>
</tr>
</tbody>
</table>
The region flow is from the Northwest towards Southeast direction toward Lavaca Bay. Localized pumping and geology will alter the flow paths and may increase contaminant travel times. In order to establish site-specific hydraulic gradients which are fundamental to any groundwater quality monitoring program, it is recommended that water level monitoring activities be started in earnest within the MAI.

**Water Quality Information**

Synoptic water quality data from a set of 20 wells in and around the proposed CO₂-EOR site was performed by Hilcorp Inc. in 2012 and reviewed by Daniel B. Stephens and Associates (DBSA, 2013). The 20 monitoring wells are depicted in Figure 4 along with oil and gas wells in the county. A total of 10 parameters, Fluoride (F), Chloride (Cl), Nitrite, (NO₂), Bromide (Br), Nitrate (NO₃), Sulfate (SO₄), Orthophosphate (PO₄), Carbon dioxide (CO₂), pH and specific conductance (EC) were measured and total dissolved solids (TDS) was inferred from specific conductance measurements.
Daniel B. Stephens and Associates Inc. evaluated the water quality data submitted by Hilcorp Inc. and regional (Jackson county-wide) data available from the Texas Water Development Board and concluded that values for six constituents (F, Cl, Br, NO3, TDS and pH) were elevated near the site when compared to water quality data available from TWDB for Jackson County. There is no well construction information (including well depths and screening intervals) provided for these 20 wells and as such it is difficult to make a rigorous comparison. Specific concerns associated with synoptic monitoring data include:

1. Lack of well construction information, particularly the absence of well depths and screening interval information make it difficult to tell whether the data are from Chicot, Evangeline or other aquifer formations.
2. The sampling conditions were not clear. Are the wells being used for groundwater production or simply monitoring? How was the system equilibrated prior to sample collection?

3. The analysis was largely focused on anions and did not include information on major cations such as Na, Ca, Mg, K, which is essential to perform charge balance calculations and evaluate the importance of trace constituents.

4. The analysis did not include any trace mineral constituents that are likely to dissolve into water when carbon dioxide gets added to it. It is important to document trace mineral constituents even if these constituents are currently below detection limits as it enables the assessment of any potential CO₂ excursions into shallow aquifers.

5. As the sampling is synoptic, it is not possible to evaluate any time trends or changes in water quality.

6. There is no water level measurements presented. This information is important to evaluate local groundwater flow directions, assess geochemical evolution of groundwater and identify likely movement of chemical constituents both within and off site.

7. Figure 4 also depicts that the wells are localized and do not fully cover the monitoring area of interest.

The monitoring data available from Texas Water Development Board (TWDB) was also used to infer water quality conditions near the site. A total of 140 wells with either water level and/or water quality data were identified by querying the TWDB Database at the time of the evaluation by DBSA. Of these
wells, two wells lacked well depth information and as such were discarded during further analysis. Screening information on these wells was sparse and as such, it was assumed that the wells were screened in the bottom section of the casing and borehole as this is generally the case. These monitoring wells were compared to aquifer thickness data (Chowdhury et al., 2004) to identify the aquifer in which they were completed. A total of 18 wells (12 Chicot and 6 Evangeline) were located within the MAI and are highlighted below in Figure 5.

![Figure 7: Location of Groundwater Quality Monitoring Wells monitored by the Texas Water Development Board](image)

Water quality data for bulk parameters, major cations and anions were extracted from the 18 wells within the MAI and schematically depicted in Figures 8-11. Note that the higher variability in Chicot
could at least partially attributable to a larger dataset (12 wells which range in depth from 26 feet – 500 feet). The Evangeline wells are more localized and available wells are all approximately 1250 feet deep.

![Graphs of pH, TDS, Total Alkalinity as CaCO3, and Total Hardness as CaCO3 for Chicot and Evangeline wells]

*Figure 8: Bulk Water Quality Characteristics in the MAI (All concentrations are in mg/L and Total Alkalinity and Total Hardness are expressed as mg/L as CaCO3)*
As can be seen from Figure 7, sodium is the major cation in both the Chicot and Evangeline Aquifers and this result is to be expected due to the proximity of the site to the Gulf of Mexico. Chloride is the dominant anion in the Chicot Aquifer again pointing towards the influence of marine aerosols. The relatively higher bicarbonate concentration in the Evangeline aquifers could be attributed to dissolution of caliche (calcium carbonate) sediments in the aquifer (Uddameri et al., 2014b). This relatively higher level of bicarbonate also manifests in the higher total alkalinity measurements found in the Evangeline aquifer which in turn also results in the pH of the Evangeline Aquifer water to be more alkaline (8.0 – 8.5) than the Chicot Aquifer water. While the data available are sparse, the analysis of major ions in the
MAI indicate that the geochemistry of the two aquifers are likely to be different and as such any accidental introduction of carbon dioxide will manifest in different water quality effects in Chicot and Evangeline Aquifers. Therefore, to the extent possible, both these aquifers must be monitored separately.

*Figure 10: Major Anion in the MAI (All concentrations are in mg/L)*

Sufficient data for trace constituents were not available to separately evaluate their chemical characteristics in different aquifers. In addition, the data was sparse for many chemical constituents within the study area. As such, data available within the Jackson County were aggregated to obtain
preliminary insights with regards to chemical characteristics. The observed concentrations of trace constituents in the Gulf Coast Aquifer within Jackson County TX are depicted in Figures 12-14.

Figure 11: Concentrations of Minor Cations and Anions in the Gulf Coast Aquifer – Jackson County, TX. (Note the data are not specific to MAI).
Figure 12: Concentrations of Trace Constituents in the Gulf Coast Aquifer – Jackson County, TX. (Note the data are not specific to MAI).
While a regional-scale evaluation of trace constituents provides an initial understanding of the observed concentration variability, the lack of stratified site-specific data is certainly a limiting factor. It is recommended that site-specific measurements of trace constituents be carried out to properly establish baseline values in the MAI. As concentrations of trace constituents are altered when CO$_2$ is introduced into freshwaters, it is recommended these constituents be monitored on a regular basis and with increased frequency when CO$_2$ intrusion into the shallower freshwater is confirmed.

Placement and Number of Monitoring Wells
The network of groundwater monitoring wells (i.e., monitoring network) at a CO$_2$-EOR site must be able to identify potential contamination to groundwater resources quickly so that corrective actions can be taken to keep the impacts localized around the source and prevent further spreading. The risks
associated with carbon sequestration are not fully understood and several concerns exist particularly of contamination to the regional aquifer (i.e., adjacent land-owner’s groundwater). A larger network extending beyond the CO₂-EOR site can provide sentinel wells to indicate regional-scale impacts to the groundwater resources. Thus, the monitoring network must be designed and develop sufficient geographic scope and density to satisfy the objectives of 1) identifying any regional-scale impacts on groundwater resources and immediately identifying any incursions of fluids into the groundwater resources within the CO₂-EOR site.

The monitoring network at the CO₂-EOR site will be denser and must contain sufficient number of wells to detect potential incursions of CO₂, brine and other chemicals from the deeper reservoirs into shallower groundwater aquifers. Clearly, artificial penetrations and natural faults located at and in the vicinity of the CO₂ Sequestration and Enhance Oil Recovery site are weak spots for leakage and as such the likely location of contamination. Therefore, monitoring efforts must focus around these potential weak-spots. However, the chemicals introduced into the aquifers will travel downgradient. In addition, advection will cause contaminants to be transported by diffusion and dispersion mechanisms as well as undergo biochemical reactions and inter-phase partitioning. Any plumes created due to contaminant transport provide useful clues for placement of monitoring wells at a CO₂-EOR sites. Two and three dimensional point source models (Wilson and Miller, 1978; Wexler, 1992) can be used to delineate and rank the land within the study area with regards to contamination potential. Simple and straightforward approaches are often deemed sufficient for establishing groundwater monitoring plans (Hansen, 1999) and the use of two- and three-dimensional analytical solutions for monitoring network design at contaminated sites is a well-established practice in the industry (Aziz et al., 2003).

Geostatistical and statistical approaches are commonly used to design groundwater monitoring network configurations (Issak and Srivastava, 1989, Nunes et al., 2004). In the geostatistical approach, the spatial correlation of a variable of interest is modeled using a semi-variogram. A theoretical semi-variogram is
fit to available empirical data and then can be used to interpolate values as well as estimate the variance (error) associated with the predictions. In particular, once the variogram is defined, the prediction error is simply a function of the network configuration. This aspect of network configurations can be exploited to identify an optimal network design from a set of potential network configurations (Ahmed, 2004). The approach adopted for this paper is as follows: 1) The area of interest is divided into a set of uniform grid cells. 2) Existing data in the vicinity of the site is used to develop a theoretical variogram for the constituent(s) of interest and used to fit a theoretical variogram. 3) Several candidate networks (set of existing and new wells) are selected based on conditions at the site and with discussions with stakeholders. 4) The prediction error in each grid is computed for each of the candidate network using kriging techniques (Issak and Srivastava, 1989). 6) The network with the lowest overall predictive error is selected as the initial design. 7) The predictive errors are then used to refine the network to further reduce errors and add additional redundancy near critical points (artificial penetrations and natural openings) with greater susceptibility. When there are multiple aquifers overlying the CO$_2$-EOR site, the process must be carried out separately for each aquifer stratum.

Geostatistical approach was used to evaluate whether the 20 well network proposed by Hilcorp Inc., (DBSA, 2013) is sufficient to evaluate water quality changes within the MAI. An equally spaced grid of (1 mile x 1 mile) was overlaid over the study area (see Figure 3). The synoptic total dissolved solids data collected by Hilcorp. Inc., was used to develop an empirical variogram and perform ordinary kriging (Issak and Srivastava, 1989). An exponential variogram with no nugget (partial sill = 858844.5 and a range of 1490 m) was selected as the final theoretical variogram model based on cross-validation errors. The range of theoretical variogram is close to 1600 m (1 mile) and as such the grid points contain minimally redundant information.
Figure 15: Error Variance for Total Dissolved Solids (TDS) based on the Proposed 20 Well Monitoring Network

Ordinary Kriging was carried out to estimate the prediction error variance, which is depicted in Figure 15. As can be seen, the prediction errors are lower where the wells are present but the current configuration of 20 wells is not sufficient and leads to very high predictive errors within the MAI.

The prediction error variance depends only upon the theoretical variogram and the configuration of the monitoring network and as such new predictive error maps can be generated for alternative monitoring network configurations. Spatially balanced sampling designs map two-dimensional space into a one-dimensional space and thereby create an ordered spatial address and random sampling of these spatial addresses leads to a spatially well-balanced designs (Stevens and Olsen, 2004). Spatially well-balanced designs tend to minimize clustering and other non-random effects and as such potentially lead to sampling strategies that offer minimal redundancy.
Spatially balanced configurations containing 20, 30 and 50 wells were generated and their corresponding predictive variances computed. The error maps corresponding to various designs are shown in Figures 16 – 18.

Figure 16: Error Variance for Total Dissolved Solids (TDS) based for Spatially-Balanced 20 Well Monitoring Network
Figure 17: Error Variance for Total Dissolved Solids (TDS) based for Spatially-Balanced 30 Well Monitoring Network
The summary statistics for prediction error variances corresponding to various network configurations are summarized in Table 3.

**Table 3: Summary Statistics for Error Variances under different Network Sizes and Configurations**

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Proposed 20 Well Monitoring Network</th>
<th>20 Well Balanced Monitoring Network</th>
<th>30 Well Balanced Monitoring Network</th>
<th>50 Well Balanced Monitoring Network</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>341700</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25&lt;sup&gt;th&lt;/sup&gt;</td>
<td>976700</td>
<td>766100</td>
<td>729300</td>
<td>0</td>
</tr>
<tr>
<td>50&lt;sup&gt;th&lt;/sup&gt;</td>
<td>1019000</td>
<td>803900</td>
<td>758000</td>
<td>715000</td>
</tr>
<tr>
<td>75th</td>
<td>1026000</td>
<td>835500</td>
<td>784250</td>
<td>727400</td>
</tr>
<tr>
<td>Max</td>
<td>1029000</td>
<td>890600</td>
<td>865800</td>
<td>794400</td>
</tr>
</tbody>
</table>

Results presented in Figures 16 - 18 and Table 3 indicate that the proposed network is highly clustered and switching it a spatially well-balanced design without changing the number of wells leads to
significant reduction in predictive errors over the entire monitoring area of interest. The spatially well-balanced monitoring network is still able to predict relatively well within the proposed West Ranch site where CO$_2$-EOR operations are proposed but marginally improve the prediction accuracy in outlying areas within the MAI.

Results in Table 3 also indicate that increasing the network size leads to an improvement in the prediction accuracy. However, spatially balanced designs result in more uniform distribution of the error variances within the MAI. The median improvement between a well-balanced 20 well configuration versus a 30 well configuration is 4590 units per well. On the other hand, the median improvement going from 30 well to a 50 well network yields 2150 units/well. As such, increasing the well density introduces redundancy and yield only marginal improvements. Based on the analysis a 30 well network (retaining 20 wells proposed by Hilcorp) and adding 10 additional wells may be reasonable initially as it maintains a high level of redundancy near the CO$_2$-EOR operations but also improves sampling resolution in the vicinity of the site. It is however important to recognize that the Hilcorp well data used in this analysis does not account for vertical stratification (i.e., does not differentiate between Chicot and Evangeline Aquifers). Ideally, having a similar network configuration (30 wells each) in Chicot and Evangeline aquifers would be optimal.

There are currently no wells in the Jasper Aquifer or Burkeville Confining layer. These units are closer to the CO$_2$-EOR operations and as such as a greater risk of exposure to potential excursions. While the groundwater in the Jasper Aquifer is likely brackish and currently not used, the Texas Legislature has recognized the importance of brackish groundwater resources for the future sustainability of the state. Recent legislation (House Bill 30) mandates that the brackish groundwater resources be quantified and efforts are underway to do so in the Gulf Coast aquifer (Mace, 2015). Monitoring groundwater resources in Jasper Aquifer should therefore be a goal and the feasibility of installing a new monitoring well or restructuring an existing oil and gas well should be explored.
Summary and Recommendations

The overall goal of this study was to develop a framework for monitoring groundwater at a proposed CO₂-EOR site in Jackson County, Texas. The groundwater monitoring activities proposed here are intended to complement pressure and other related measurements in the producing reservoir. Groundwater monitoring adds another layer of safety to the operations further improves the reliability of the proposed sequestration activities. Groundwater monitoring may also help improve public trust in the project. Hydrogeochemical information in the vicinity of the West Ranch, CO₂-EOR site was also evaluated as part of this study. The goal of the evaluation was to identify data that are available, evaluate limitations of existing data, identify critical data gaps and obtain preliminary insights related to geochemical variability to be expected at the site. The major findings associated with this data evaluation include:

1. There are over 200 oil and gas wells at the site including 87 plugged and 34 temporarily abandoned wells. While these wells are regulated by Texas Railroad Commission and currently do not appear to pose any problems, they provide a conduit (artificial penetration) between deeper oil-bearing and shallower water bearing reservoirs. As such, it is recommended that groundwater monitoring wells be placed near clusters of oil and gas wells.

2. The Chicot and Evangeline Aquifers are currently being used in Jackson County in the vicinity of the West Ranch site. However, existing wells do not fully penetrate the aquifers. Deeper wells will likely be placed for future water development. Considerable variability in water quality is noted with available data. As such, stratified sampling within each aquifer (i.e., using wells penetrating different depths) is recommended as a monitoring goal.
3. The water well database maintained by the Texas Water Development Board identifies at least 90 wells in the Monitoring Area of Interest (MAI), which is a 5-mile radius buffer around the West Ranch Site. However, water quality data is only available in 18 of these wells (12 Chicot Aquifer and 6 Evangeline Aquifer).

4. There are currently no wells in the Burkeville Confining Unit or the Jasper Aquifer. The water in these formations are likely to be brackish and occur at considerable depth. While the current demands near the site make the use of these aquifers unlikely, there is a growing interest in using brackish groundwater resources and as such the potential for use does exist in the future. Furthermore, any accidental leaks of CO$_2$, brine and other fluids from the reservoir will first enter the Jasper portion of the Gulf Coast aquifer. As such, installation of monitoring wells in these formations should be a monitoring goal.

5. The water quality data from 20 wells sampled by Hilcorp Inc., in 2012, provides site specific information on groundwater geochemistry. However, the results are not aquifer specific which makes it difficult to evaluate baseline conditions in Chicot and Evangeline Aquifers. While the data provides a general idea of potential groundwater quality at the site, analysis of available geochemical data from TWDB indicates that the Chicot and Evangeline Aquifers have different geochemical signatures. As such, it is recommended that these aquifers be monitored separately.

6. It appears that the concentrations of several monitored constituents at the West Ranch Site are higher than what is observed elsewhere in Jackson County. However, additional analysis is not
possible due to data limitations. It is recommended that well construction data including but not limited to well depths, screening intervals, casing materials and drilling dates be compiled for these wells to place results in proper perspective.

7. The dataset of water quality information sampled from the West Ranch (DBSA Study) focuses primarily on anions and bulk geochemical parameters. Major cations, other trace elements, and organic constituents must also be analyzed to allow complete and comprehensive characterization of water quality at the site. The absence of cation data precludes charge balance calculations and properly interpreted geochemical characteristics at the site.

8. There are several analytes of interest that have not been monitored either on-site or in the vicinity. These parameters include methane, oil and grease, total petroleum hydrocarbons (TPH), Diesel Range Organics (DRO), isotopic data as well as tracers such as perfluoroethenes (PFEs) that could be used to detect brine, CO₂ and hydrocarbon leaks.

9. The aquifer mineralogy of the Gulf Coast Aquifer System is poorly understood and site-specific mineralogical data does not exist. There is a growing body of literature that indicates that mineral-water interactions are affected by incursions of carbon dioxide into aquifers. As such, mineral characterization at the site should also be a monitoring goal.

10. The proposed monitoring network by the Hilcorp Inc. has good spatial coverage within the site, but is not capable of detecting water quality alterations in the neighboring areas. The lack of stratification limits the suitability of the proposed network even to monitor potential water quality alterations within the site. Preliminary network configuration analysis indicates that a 30
well network per aquifer strata (Chicot and Evangeline Aquifers) could provide optimal coverage.

References


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