MONITORING AND NUMERICAL MODELING OF SHALLOW CO_2 INJECTION, GREENE COUNTY, MISSOURI

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ABSTRACT

The project titled Monitoring and Numerical Modeling of Shallow CO_2 Injection, Greene County, Missouri provided training for three graduate students in areas related to carbon capture and storage. Numerical modeling of CO_2 injection into the St. Francois aquifer at the Southwest Power Plant Site in Greene County, Missouri indicates that up to 4.1×10^5 metric tons of CO_2 per year could be injected for 30 years without exceeding a 3 MPa differential injection pressure. The injected CO_2 would remain sequestered below the top of the overlying caprock (St. Francois confining unit) for more than 1000 years. Geochemical modeling indicates that portions of the injected CO_2 will react rapidly with trace minerals in the aquifer to form various solid carbonate mineral phases. These minerals would store significant portions of injected CO_2 over geologic time scales. Finally, a GIS data base on the pore-fluid chemistry of the overlying aquifer system in Missouri, the Ozark aquifer, was compiled from many sources. This data base could become useful in monitoring for leakage from future CO_2 sequestration sites.

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EXECUTIVE SUMMARY

This report describes results of the project: Monitoring and Numerical Modeling of Shallow CO_2 Injection, Greene County, Missouri. The project included three main tasks related to carbon capture and storage: student training in numerical modeling, instrumentation and monitoring and construction of a GIS data base of pore-fluid chemistry within Missouri aquifers. The second task was amended to emphasize geochemical modeling to investigate the fate of CO_2 injected into the St. Francois aquifer of Missouri.

To complete the first task, related to numerical modeling, a student research assistant (RA) first analyzed a series of hydraulic tests measuring the hydraulic conductivity and permeability of formations within the St. Francois aquifer system at the Southwest Power Plant Site in Greene County, Missouri. These tests had been completed earlier as part of the Missouri Shallow Carbon Sequestration Project conducted by City Utilities of Springfield, Missouri. Permeability values obtained from these tests were used as input parameters in a multiphase flow model to predict the injectability and long-term behavior of CO_2 sequestered within the St. Francois aquifer. Based on model results, a differential injection pressure of 3 MPa could sequester approximately 4.1×10^5 metric tons per year over a 30 year period. After 1000 years of simulation time all of this CO_2 remained confined below the top of the caprock (the St. Francois confining unit) above the injection zone due to its ultra-low permeability.

A second RA completed a set of geochemical modeling simulations of injected CO_2 to complete the second task. These results indicate that the St. Francois aquifer contains mineral constituents that will react rapidly with injected CO_2 to form solid-phase carbonate minerals, which will remove some of the injected CO_2.

A third RA gathered geochemical data from various sources, including many unpublished reports, to compile a GIS data base of pore-fluid chemistry and its spatial variation for Missouri's Ozark aquifer, which overlies the St. Francois aquifer system. This data base has been delivered to the Missouri Division of Geology and Land Survey to assist that agency in future investigations. Data are scarce for areas where the underlying St. Francois aquifer is saline and consequently could be used for CO_2 sequestration, but an expanded version of the data base could be useful in future monitoring for changes in chemistry within the Ozark aquifer as a result of CO_2 injection into the underlying St. Francois aquifer.

I. INTRODUCTION

This document is a report of activities completed by Missouri State University (MSU) investigators for the project: Monitoring and Numerical Modeling of Shallow CO_2 Injection, Greene County, Missouri. This project was funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) as part of their effort to promote education and training of future scientists and engineers for CO_2 capture and storage (CCS). The project was also designed to supplement and use data from another and concurrent NETL-funded project: the Missouri Shallow Carbon Sequestration Project, conducted by City Utilities of Springfield, Missouri.

The project entailed three main tasks explicitly or implicitly related to student training in CCS:

Task 2.0. Student Training in Numerical Modeling.
Task 3.0. Instrumentation and Monitoring.
Task 4.0 . Construction of a GIS Data Base of Pore-Fluid Chemistry within Missouri Aquifers.

Three graduate students (RAs), under the direction of the project PIs, completed work associated with each respective task to promote their training in CCS.

The remainder of this report describes these tasks in more detail, along with the activities completed by MSU researchers. The following chapters describe the methods and rationales for each task, followed by relevant results. These chapters also describe any changes or adaptations to the original work plan that were necessitated by changes in the Missouri Shallow Carbon Sequestration Project and the nature and amount of data available.

II. Methods

Task 2.0. Student Training in Numerical Modeling.

Background and General Procedures

PI Rovey recruited and trained a graduate student (Stephanie Stratton) Research Assistant (RA) in the use of multiphase flow models to simulate CO_2 injection into the St. Francois aquifer at the City Utilities Southwest Power Plant Site (SWPP) in Greene County, Missouri. PetraSim®, a 3D graphical interface of the TOUGH2 multiphase flow model was used for this project. Additionally, RA Stratton developed proficiency in the use of an analytical modeling program (AQTESOLV®) in analyzing hydraulic-test data at the SWPP site to provide permeability values used in the model.

The St. Francois aquifer in this area includes two sandstones with relatively high permeability, the Reagan Sandstone and the underlying Lamotte Sandstone, separated by dolomitic fine-grained siltstone and shale of the Bonneterre Formation. The aquifer is confined above and below by low permeability units, the shale-rich St. Francois confining unit (Derby-Doerun and Davis Formations) and Precambrian granites, respectively (Table 1). The modeling simulated CO_2 injection individually into the Reagan and Lamotte Sandstones.

Table 1. Hydrostratigraphy of the St. Francois aquifer and confining unit in Greene County, Missouri. Modified from Emmett et al. (1978).

Geologic System	Formation	Lithology	Hydrologic Unit
Cambrian	Derby – Doerun Formation	Interbedded shale And dolomite	St. Francois Confining Unit
	Davis Formation	Interbedded shale and limestone	
	Reagan Sandstone	Sandstone, grading downward to siltstone with shale interbeds	St. Francois Aquifer
	Bonneterre Formation	Glauconitic dolomitic siltone and shale	
	Lamotte Formation	Arkosic conglomeritic sandstone at base, grading upward to sandstone and then shale and siltstone near top.	
Precambrian	Unnamed	Granite, jointed and weathered near top	Basement Confining Unit

The most important parameters for simulating CO_2 injection are the permeability and porosity of the aquifer and confining layers. These values were taken or calculated from tests completed at the SWPP site in Greene County, Missouri (Figure 1) as part of the Missouri Shallow Carbon Sequestration Project. Porosity averages for the various strata were taken from both porosimeter measurements and thin-section point counts (Dunn-Norman et al., 2013, Berger, 2011). Permeability was calculated from single-well pumping tests and pressure-injection tests as discussed below.

Pumping Tests

Multiple single-well pumping tests were completed within the St. Francois aquifer at the SWPP as part of the Missouri Shallow Carbon Sequestration Project. RA Stratton re-analyzed two of these tests, during which pumpage was isolated by packers from within the Reagan and Lamotte Sandstones, respectively. Pumpage rates and drawdowns in water level from these tests were entered into the analytical modeling program AQTESOLV® to calculate bulk transmissivity, hydraulic conductivity, and storativity of the respective formations. Hydraulic conductivities are calculated by dividing the transmissivity by aquifer thickness, and permeability values are then calculated from the hydraulic conductivities, based on the standard density and viscosity of water.

Pumping test results were analyzed using three standard procedures or solutions in succession: the Cooper-Jacob (semilog) method, the Theis solution and the Hantush-Jacob (leaky) solution. The Cooper-Jacob method provides a transmissivity value based on the late portion of the semilog slope of drawdown versus time. This method, however, does not provide an accurate estimate of storativity for single-well tests. Next, the same data were analyzed again using the Theis solution, which is based on the match of the drawdown data on a log-log plot with a standard (Theis) curve. However, the Theis solution does not account for water within a borehole prior to pumping, and this causes a large deviation ("borehole storage effects") between measured and theoretical values at early time for a single-well test. At later times, borehole storage effects become insignificant, and the field measurements can be matched to the standard Theis curve, but with a range of transmissivity and storativity values. To calculate a unique set of values, the transmissivity from the Cooper-Jacob analysis is entered as an initial "seed" value in the AQTESOLV® program and the storativity value is adjusted to improve the visual match between the measured and theoretical curves. In practice this best match is achieved by iteration with small additional changes in transmissivity.

Both the Cooper-Jacob and Theis methods ignore leakage from the confining layer into the aquifer during the pumping test. Consequently, these methods may overestimate transmissivity. This happens, because water which was supplied to the aquifer in the vicinity of the well by leakage is attributed to lateral flow within the aquifer from a greater distance. In practice, leakage is detected by an inability to match the measured rate of decline in drawdown near the end of the test with the decline predicted by the Theis solution. Therefore, the last step of the pumping-test analysis was to test and correct for leakage by matching the field data to the Hantush-Jacob method.

Pressure-Injection Tests

Pressure-injection tests measure the hydraulic conductivity and permeability in the vicinity of a borehole by isolating a vertical interval between inflatable packers. The standard method is termed an open test: water pressure between the packers is increased by rapidly adding water within drill rods above the upper packer, and water then flows into the borehole through perforations in the drilling rods within the packed interval and into the formation. The rate at which the pressure and water level recovers to the initial or static value (before adding water) is proportional to the hydraulic conductivity. This general procedure was used for determining permeability of the confining intervals: the overlying St. Francois confining unit, as well as the Bonneterre Formation, which is between the two higher-permeability sandstones.

If the hydraulic conductivity is low enough, standard pressure tests are ineffective and only measure an upper bound to the true value. In these cases (most of the tests here) the hydraulic conductivity was determined with a "shut-in" test. For a shut-in test water is added to the drill rods as before, which pressurizes the water within the packed interval, but then a valve atop the upper packer is closed, which isolates the pressurized water within the borehole between the packers from the overlying water within the drill rods. In this case any water which flows into the formation causes pressure to drop within the isolated borehole, which then allows a minute expansion of the remaining water to balance the volume that enters the formation. Because an extremely small amount of flow out of the borehole and into the formation causes a large drop in pressure, such tests can measure ultra low values of hydraulic conductivity.

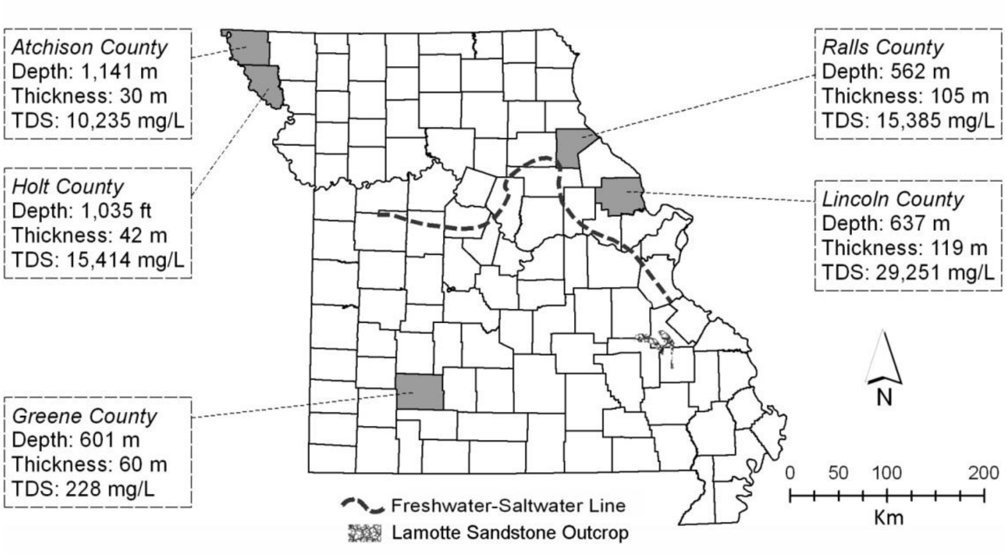
A series of pressure-injection tests were completed at the SWPP site for the Missouri Shallow Carbon Sequestration Project. RA Stratton analyzed 15 of these tests within the confining units, the Derby-Doerun, Davis and Bonneterre Formations. These tests were also analyzed with AQTESOLV® using the standard Hvorslev method and, where possible, the deconvolution method of Peres et al. (1989). The deconvolution method is useful for determining whether drilling has disturbed the permeability near the borehole.

Task 3.0. Instrumentation and Monitoring.

The original plan included monitoring the downhole pressure, CO_2 migration, tracer migration and geochemical changes within the St. Francois aquifer during a trial injection of CO_2 at the SWPP site in Greene County, Missouri. The trial injection was one of the planned tasks for the concurrent Missouri Shallow Carbon Sequestration Project. Additionally, we planned to have the RA associated with this task undertake geochemical modeling to simulate observed changes of the pore-fluid chemistry during the monitoring period, as part of the thesis project. However, the pore-fluids at the SWPP site turned out to be too low in salinity to obtain a permit for CO_2 injection. Therefore geochemical modeling, in a predictive sense, became the main focus of this task.

Co-PI Biagioni recruited and trained a graduate assistant (RA) Nelson Rono in the use of geochemical models to simulate the chemical effects of CO_2 injection and sequestration. The Geochemist's Workbench® model (GWB) was used to simulate the effects of CO_2 injection into the St. Francois aquifer system at five locations in Missouri (Figure 1). These locations were chosen based on available data and proximity to large coal-fired electrical generating plants, which would be plausible sites for CO_2 sequestration. The GWB model calculates the equilibrium concentration of dissolved pore-water chemical species or ions in contact with specified solid (mineral) phases, given initial starting concentrations, including the fugacity of CO_2 and the concentration of the dissolved ions. The model also predicts the amount and types of mineral dissolution/precipitation required to reach chemical equilibrium. The reaction rates, or time required to dissolve/precipitate a given mass of solid phase can also be calculated, given kinetic rate constants.

Figure 1. Location of geochemical modeling sites showing the depth to top of the Lamotte Sandstone, its thickness, and TDS of the formation water within the St. Francois aquifer. The dashed line depicts the freshwater-saltwater transition boundary



The following parameters are needed to model the effects of CO2 injection within a geologic medium:

1. Depth (and hydrostatic pressure) to the injection zone.
2. Downhole temperature.
3. Pore-fluid chemistry.
4. Mineral composition of the geologic medium.

These values were gathered from both published and unpublished sources. The mineral composition of the St. Francois aquifer at various sites was taken from earlier work completed for the Missouri Shallow Carbon Sequestration Project (Nondorff, 2010; Berger, 2011) and from unpublished data archived at the Missouri Division of Geology and Land Survey (DGLS). The rest of the data was obtained from well logs and unpublished DGLS reports, mostly during RA Rono's internship with that agency.

Task 4.0. Construction of a GIS Data Base of Pore-Fluid Chemistry within Missouri Aquifers.

Background

Some of the most important questions in assessing sites for shallow carbon sequestration in Missouri are: (1) What are typical water chemistries within strata overlying the injection zone, and (2) what effect would leakage have on those chemistries, i.e. how could leakage be recognized?

Therefore, co-PI Gouzie recruited and trained a graduate research assistant (RA), Nathan Diaz, in Task 4.0, the development of a GIS database and maps of geochemical facies within various strata in Missouri.

Three specific sub-tasks were associated with this effort:

1.) Obtain and sort local municipal and industrial wells within the aquifer overlying the anticipated injection interval at the SWPP site by stratigraphic unit.

2.) Collect and analyze similar data for other sites in Missouri regions with potential injection zones, utilizing the state geological survey (DGLS) data base.

3.) Enter all of the collected data into a GIS data base and generate appropriate maps of aquifer geochemical parameters.

Study Area

The Ozark Plateaus aquifer system, from the surface downward, includes: the Springfield Plateau aquifer, Ozark confining unit, Ozark aquifer, St. Francois confining unit, St. Francois aquifer, and Precambrian aged Basement confining unit (Table 1).

This task required more detail concerning the stratigraphy of the Ozark aquifer (Table 2). From oldest to youngest the formations within the Ozark aquifer are the Cambrian aged Potosi Dolomite, Cambrian aged Eminence Dolomite, and Ordovician aged Gasconade formation (including the Gunter Sandstone Member), Roubidoux Formation, Jefferson City Dolomite, and Cotter Dolomite.

Table 2. Hydrostratigraphy of the Ozark aquifer in Greene County, Missouri. Modified from Emmett et al. (1978).

Geologic System	Formation	Lithology	Hydrologic Unit
Ordovician	Cotter Dolomite	Dolomite with interbedded shale laminae	Ozark aquifer
	Jefferson City Dolomite	Dolomite with interbedded shale laminae	
	Roubidoux Formation	Sandstone with interbedded dolomite	
	Gasconade Formation	Porous dolomite with a sandstone (Gunter Member) at base	
Cambrian	Eminence Dolomite	Porous to cavernous dolomite	
	Potosi Dolomite	Porous to cavernous dolomite	

Hydraulic conductivity tends to increase downwards within the Ozark aquifer from the Cotter Formation to the Potosi Formation, and the available data in Greene County indicated that chemical concentrations within the pore water might vary with depth as well (Emmett et al., 1978). These differences may be related to variation in aquifer chemistry, differences in residence time and/or recharge locations.

Data Collection

This study is focused upon determining which geochemical parameters can be used to determine if carbon dioxide has leaked upward into the Ozark aquifer after anticipated injection into the underlying St. Francois aquifer. Existing water-quality information was obtained from the United States Environmental Protection Agency (U.S. EPA) Safe Drinking Water Information System (SDWIS) database, the United States Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) database, and the Missouri Department of Natural Resources (MoDNR) well database. Information pertaining to well construction, geologic logs, water levels, and well yields was obtained from the MoDNR wells and LOGMAIN database. The aggregation of these data into a geodatabase was performed as the first two steps of this task of the overall project.

While working as an intern at the Missouri Geologic Survey, RA Diaz utilized the Missouri Department of Natural Resources files and file access to USEPA SDWIS database and the USGS NAWQA database. These sources were combined with in-house data files (including paper files at the Missouri Geologic Survey), a database was developed which would allow retrieval and processing of groundwater geochemistry data from the Ozark Plateaus Region across much of Missouri.

In building the database, reported well locations were originally referenced to the North American Datum of 1983 (NAD83), but were projected to Universal Transverse Mercator 15N (UTM 15N). Well locations that fell outside of the general extent of the Ozark Plateau Province

(Imes, 1990a, 1990b; Imes and Emmett, 1994; Pope et al., 2009) where also considered to be part of the aquifer system.

Routine water-quality samples had been collected by state and federal agencies from wells withdrawing water from the Ozark aquifer as an attempt to better understand the geochemistry of the aquifer. To maximize spatial distribution, a combination of the aforementioned government agencies' databases was used to minimize spatial data gaps. Data were stored and managed within a customized geodatabase shapefile that displays individual wells as discrete object features. The geodatabase contains information pertaining to county location, the reporting agency, various water-quality parameters (e.g. Ca^{2+}, field-measured pH), and geologic formation data from well logs. As a public product from this project, the database was delivered to the Missouri Geologic Survey for their future use in evaluating water quality conditions beneath the state.

Data Processing

To minimize skewing of data, wells used for graphical display of geochemistry were selected, based on their proximity and two hydrologic parameters. First, geologic formation data was used exclude all wells that do not receive water exclusively from the Ozark aquifer. The remaining wells were then assigned to one of three casing scenarios: an upper Ozark aquifer well (Cotter/Smithville-Powell to Jefferson Formation); a lower Ozark aquifer well (Roubidoux to Potosi Formation); or an upper and lower Ozark aquifer well (open to all or almost all formations within the Ozark aquifer).

Second, the predevelopment potentiometric surface map for the Ozark aquifer from Imes and Emmett (1994) was used to infer general flow path directions among sampled wells. Groundwater within the aquifer contains the major ions typically found in natural waters: calcium, magnesium, sodium, and potassium cations, and bicarbonate, sulfate, and chloride anions.

Due to wells being finished in more than one formation, evaluating the water-quality in detail was limited by the availability of samples from specific formations. Because of the limited availability of wells penetrating only a portion of the Ozark aquifer (more specifically, the very limited number of wells which were only open to the lowermost portion of the aquifer), it was not feasible to generate separate maps for the geochemistry of the lower Ozark aquifer and the upper Ozark aquifer as had originally been planned.

It should also be noted that, before including sample data in the following major ion maps, the accuracy of samples was evaluated by considering the charge balance, or electroneutrality conditions of a sample.

III. Results

Task 2.0. Student Training in Numerical Modeling.

Pumping Tests

Pumping test results from the upper and lower sandstones (Reagan and Lamotte, respectively) at the SWPP site are summarized in Tables 3 and 4. Transmissivity (T) and storativity (S) are calculated directly from the tests, while hydraulic conductivity is calculated by dividing Transmissivity by formation thickness. Intrinsic permeability is calculated from Equation 1 using the standard density and viscosity of water.

$$k_i = K\mu/\rho g \qquad \text{Equation 1}$$

where k_i = intrinsic permeability, K = hydraulic conductivity, ρ = fluid density, μ = viscosity of water and g = acceleration of gravity.

Table 3. Transmissivity (T) and Storativity (S) from pumping tests at the SWPP Site. Storativity is dimensionless.

Test Interval	Method				
	Cooper-Jacob	Theis		Hantush-Jacob	
	T (m^2/sec)	T (m^2/sec)	S	T (m^2/sec)	S
Reagan	4.2×10^{-5}	4.0×10^{-5}	1.8×10^{-4}	3.9×10^{-5}	5.1×10^{-5}
Lamotte	5.3×10^{-6}	4.6×10^{-6}	1.6×10^{-5}	3.9×10^{-6}	1.5×10^{-5}

Table 4. Hydraulic conductivity (K) and permeability (k_i) calculated from transmissivity values in Table 3.

Test Interval	Method					
	Cooper-Jacob		Theis		Hantush-Jacob	
	K (m/sec)	k_i (m^2)	K (m/sec)	k_i (m^2)	K (m/sec)	k_i (m^2)
Reagan	1.4×10^{-6}	1.2×10^{-13}	1.3×10^{-6}	1.1×10^{-13}	1.3×10^{-6}	1.1×10^{-13}
Lamotte	8.6×10^{-8}	7.5×10^{-15}	7.7×10^{-8}	6.7×10^{-15}	6.4×10^{-8}	5.6×10^{-15}

The various analyses give similar values for transmissivity, hydraulic conductivity and permeability. The Cooper-Jacob and Theis methods neglect leakage into the aquifer from confining layers and therefore give slightly larger values of transmissivity than the Hantush-Jacob method, which also provides a somewhat lower value of storativity. The upper (Reagan)

Sandstone is much more permeable than the Lamotte Sandstone and should be able to accommodate higher injection rates of CO_2.

Pressure-Injection Tests

Results of the pressure-injection tests are given in Table 5. The shale-rich intervals of the St. Francois confining unit generally have hydraulic conductivity values ranging from 10^{-12} to 10^{-14} m/sec and corresponding intrinsic permeabilities from around 10^{-19} to 10^{-21} m^2, based on the (standard) Hvorslev method. These are extremely low values, indicating that the St. Francois confining unit would be a highly effective barrier restricting upward migration of pore fluids (both water and gas) into overlying strata. The Peres et al. (deconvolution) method, where successful, tends to give somewhat lower values of hydraulic conductivity than the standard Hvorslev method. This difference shows that the ultra-low values obtained here are not artificially low due to borehole disturbance, or so-called skin effects. Any drilling disturbance seems to have slightly enhanced permeability in the immediate vicinity of the wellbore, probably by inducing small-scale isolated fractures.

The permeabilities obtained for the Bonneterre formation (between the Reagan and Lamotte Sandstones) ranges from approximately 8×10^{-19} to 8×10^{-18} m^2, although the upper test, with the larger value, was open to a portion of the lower Reagan Sandstone. These permeabilities are generally greater than those within the shale-rich intervals of the overlying Davis Formation, but are still small enough to impede fluid flow between the two sandstones.

Model Layers

The pumping and pressure-test results were used to assign permeability values for up to 10 model layers (Table 6). Porosity values are taken from point counts of thin sections for the Lamotte, Bonneterre and Reagan formations (Berger, 2011) and from porosimeter measurements for the Davis and Derby-Doerun Formations (Dunn-Norman et al., 2013)

The layer boundaries in Table 6 correspond to pressure-test boundaries in Table 5. Single or averaged Hvorslev values are used as bulk permeability values for layers 1-7 and 9. Pumping-test values (Hantush-Jacob method, Table 4) are used as bulk permeabilities for layers 8 and 10, which represent the Reagan and Lamotte Sandstones, respectively. The lowermost portion of the Reagan and uppermost portion of the Lamotte, have much lower permeabilities than the rest of these formations, and those intervals are grouped with lower-permeability confining units. Therefore, the measured transmissivity values in Table 6 are apportioned to a slightly thinner interval than the full formation thickness used in Table 4, meaning that the calculated bulk permeabilities for layers 8 and 10 (Reagan and Lamotte Sandstones) are slightly higher than the bulk pumping test values.

Table 5. Pressure test results.

Formation	Test Interval (depth below ground surface, m.)	Hvorslev Method		Deconvolution
		K (m/sec)	k_i (m^2)	K (m/sec)
Derby-Doerun	468.4-474.9	2.9×10^{-8}	2.6×10^{-15}	1.3×10^{-7}
Derby-Doerun	474.5-481.0	5.8×10^{-13}	5.1×10^{-20}	2.5×10^{-13}
Derby-Doerun/Davis	480.9-487.4	$< 1 \times 10^{-9}$	$< 1.8 \times 10^{-16}$	$< 1 \times 10^{-9}$
Davis	487.0-493.5	$< 1 \times 10^{-9}$	$< 1.8 \times 10^{-16}$	$< 1 \times 10^{-9}$
Davis	492.8-499.3	1.5×10^{-13}	1.3×10^{-20}	Unstable
Davis	498.9-505.4	7.5×10^{-14}	6.6×10^{-21}	Unstable
Davis	505.0-511.5	2.0×10^{-14}	1.8×10^{-21}	Unstable
Davis	511.1-517.6	1.8×10^{-12}	1.5×10^{-19}	4.1×10^{-12}
Davis	518.1-524.6	1.6×10^{-7}	1.4×10^{-14}	1.2×10^{-7}
Davis	522.3-528.6	5.8×10^{-11}	5.1×10^{-18}	8.3×10^{-13}
Davis	528.6-534.8	2.7×10^{-14}	2.4×10^{-21}	9.4×10^{-15}
Davis	534.8-541.1	3.5×10^{-12}	3.0×10^{-19}	5.5×10^{-13}
Lower Reagan/ Bonneterre	569.9-582.8	9.5×10^{-11}	8.3×10^{-18}	2.3×10^{-12}
Bonneterre	582.0-595.0	9.3×10^{-12}	8.1×10^{-19}	3.6×10^{-13}

The ability of the upper confining units (Davis and Derby-Doerun Formations) to restrict upward migration of injected CO_2 within the Reagan and Lamotte Sandstones was one of the issues assessed with the model. Therefore, the finest zonation or subdivision of the confining unit in the model was directly above layer 8, which represents the Reagan Sandstone. Model layers 4-7 correspond to single pressure-injection tests, while model layers 1-3 represent intervals with multiple pressure-injection tests. In the latter cases, the layer permeability is the harmonic mean of the individual pressure-test values. The use of harmonic means converts the various horizontal permeabilities into a single theoretically equivalent vertical permeability over that interval.

The permeability values for the confining layers are calculated from the Hvorslev values in Table 5. As mentioned previously, these values are slightly larger than the corresponding deconvolution values, meaning that the drilling probably enhanced permeability along the borehole wall relative to its undisturbed condition. Therefore, the Hvorslev values present a conservative scenario with respect to CO_2 confinement below the Davis Formation; the model predictions probably would overestimate the extent of upward migration.

Table 6. Layer properties for multi-layer simulations. See text for explanations.

Layer #	Interval from model base (m)	Formation	Intrinsic Permeability (m^2)	Porosity (%)
1	187.1-198.3	Derby-Doerun	2.6×10^{-15}	2
2	174.6-187.1	Derby-Doerun	5.1×10^{-20}	2
3	143.6-174.6	Davis	4.4×10^{-20}	2
4	139.4-143.6	Davis	1.4×10^{-14}	2
5	133.1-139.4	Davis	5.1×10^{-18}	2
6	126.8-133.1	Davis	2.4×10^{-21}	2
7	111.4-126.8	Davis	3.0×10^{-19}	2
8	79.5-111.4	Reagan	1.4×10^{-13}	12
9	28-79.5	Lower Reagan-Bonneterre-upper Lamotte	2.4×10^{-18}	4
10	0-28	Lamotte/Precambrian	8.9×10^{-15}	10

Multiphase Flow Parameters

Additional parameters are needed to simulate multiphase flow, i.e. CO_2 injection into a water-saturated medium (Table 7). Default values within PetraSim® were used for Residual Liquid Saturation, Residual Gas Saturation, and the Pore Size Distribution Index, as measured values were not available. Nevertheless, values here are commonly used for simulating CO2 migration (e.g. Preuss and Garcia, 2002), and a sensitivity analysis of these parameters showed that variations by up to a factor of two had little effect on the long-term model results. Gas entry pressures were calculated from a regression equation between permeability and measured values for CO_2 gas displacing water (Hildenbrand and Drooss, 2001). Hildenbrand and Drooss also found that gas entry pressures for CO_2 are less than those for other gas phases, so values used here will allow greater upward migration of CO_2 into the caprock during model simulations, compared to values based on other gasses, e.g. nitrogen as commonly used. Pore compressibility was calculated from a representative storativity value (5×10^{-4}) from the pumping tests using Equations 2 and 3.

$S_s = \rho_w g(\alpha + n\beta)$ Equation 2

where S_s = specific storage, ρw = density of water, g = acceleration of gravity, α = compressibility of the aquifer, β = compressibility of water,

$S_s = Sb^{-1}$ Equation 3

where S = aquifer storativity (dimensionless) and b = aquifer thickness.

The model results for long-term simulations showed little sensitivity to the input value of pore compressibility, justifying the use of a single value.

Table 7. Multiphase flow parameters. See text for explanations.

Parameter	Explanation	Value Used
Residual Liquid Saturation	Ratio of volume of liquid irreducibly trapped within the pore space upon displacement of the liquid phase by gas	0.3 (default value)
Residual Gas Saturation	Ratio of volume of gas irreducibly trapped within the pore space upon displacement of the gas phase by liquid	0.05 (default value)
Pore Size Distribution Index	Empirical function of the pore-size distribution	0.457 (default value)
Inverse of Gas Entry Pressure (Pa^{-1})	Inverse of pressure necessary to initially displace the liquid phase by the gas phase	3.3×10^{-6} (Layers 8, 10) 5.1×10^{-4} (Layers 1-7) 1.0×10^{-5} (Layer 9)
Pore Compressibility (Pa^{-1})		3.3×10^{-8}

Simulation Results

All simulations utilized a single well with injection proceeding over a 30-year duration. Simulations began with single-layer radial configurations to determine the injectability of CO_2 into the Reagan and Lamotte Sandstones under perfectly confined conditions. These were followed by multi-layer simulations to also assess the ability of the caprock (Davis and Derby-Doerun Formations) to prevent upward migration of injected CO_2. Finally a series of compositional simulations were completed to assess injectability and migration under strong regional pressure gradients.

The injectability of CO_2 depends on various hydraulic properties of the formation (i.e. permeability, porosity), but it is also proportional to the differential injection pressure, and in practice there will be some upper limit to this value. For CO_2 sequestration this is likely to be a regulatory limit related to the ability of the rock to withstand fracturing or breakdown due to the injection pressure. At the SWPP site the initial estimate of the breakdown pressure was reported to us by the contractor as approximately 6 MPa. We then assumed a safety factor of two, such that the regulatory limit would be one half of this value, or 3 MPa. A more-refined analysis, completed later, showed that this value is conservative, as the minimum breakdown pressure obtained from 10 tests within the Reagan, Bonneterre and Lamotte formations was approximately 10 MPa. Therefore, achievable injection rates, based on the same model parameters and assumptions summarized here would be higher than those listed below.

For simulated conditions, including the 3 MPa pressure limit, the single-layer radial models give maximum injection rates of CO_2 into the Reagan and Lamotte Sandstones at the SWPP site of approximately 4.1 x 10^5 and 2.1 x 10^4 metric tons per year, respectively (Table 8). These values were obtained by trial and error over a range of injection rates. Figures 1 and 2 show the simulated pressure versus distance and the CO2 saturation versus distance for injection into the Reagan Sandstone using a single-layer radial model.

Table 8. Maximum injection rates at the SWPP site. See text for explanations.

Simulation Type	Injection Formation	Maximum Injection rate (metric tons/year)
Single-Layer Radial	Lamotte	2.1 x 10^4
Single-Layer Radial	Reagan	4.1 x 10^5
Multi-Layer Radial	Lamotte	2.1 x 10^4
Multi-Layer Radial	Reagan	3.9 x 10^5
Compositional (9.8 Pa/m)	Lamotte	7.9 x 10^3
Compositional (9.8 Pa/m)	Reagan	2.1 x 10^5

Figure 2. Model simulated pressure versus distance for the Reagan Sandstone, single layer radial model. The injection rate is 4.1 x 10^5 metric tons per year over 30 years. The vertical axis (pressure) is in Pascals; the horizontal axis (distance) is in meters.

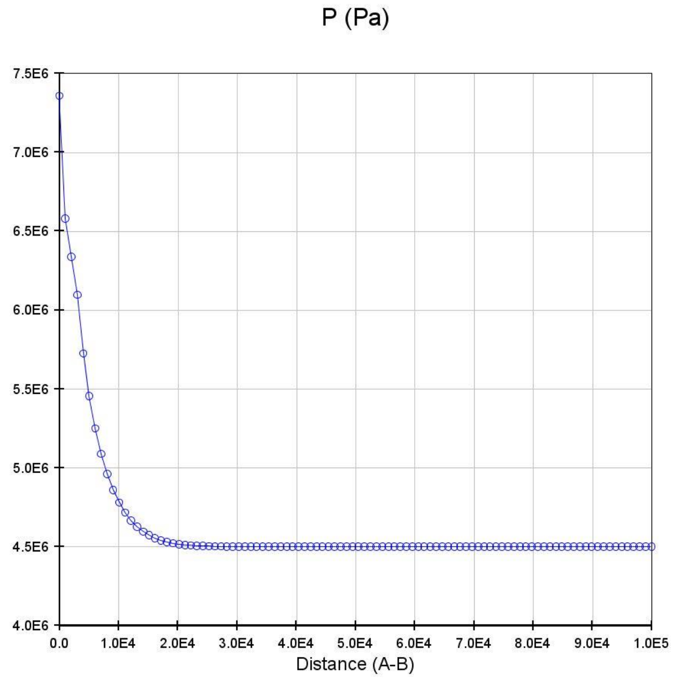
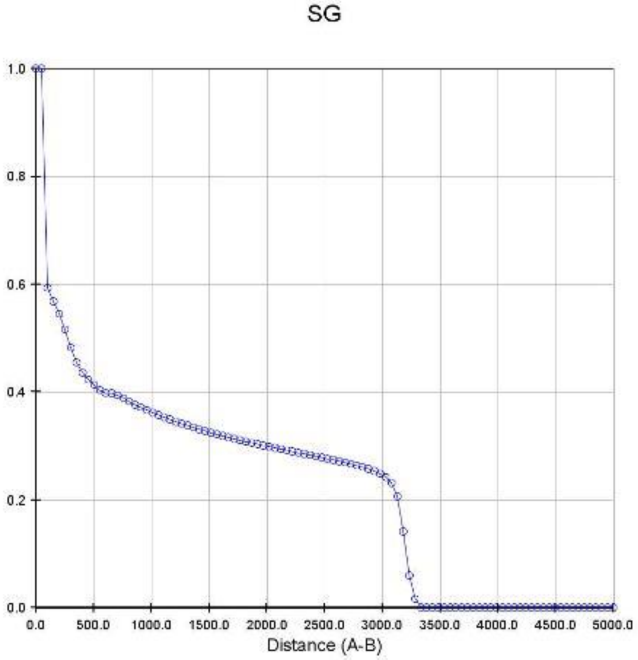


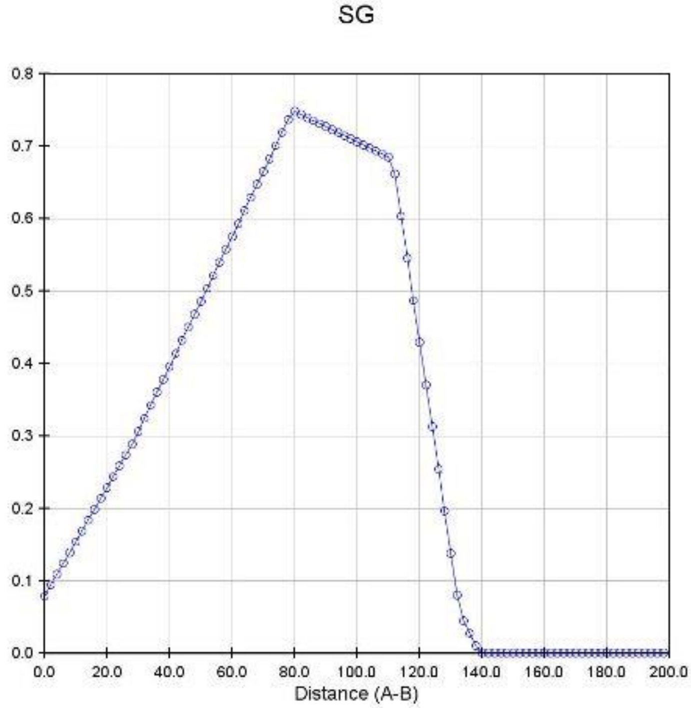
Figure 3. Gas saturation (vertical scale) as a fraction of the pore space, versus distance (meters) for injection into the Reagan Sandstone, single-layer radial model. The injection rate is 4.1 x 10^5 metric tons per year over 30 years.



The multi-layer radial models give nearly identical values of injectability (Table 8), meaning that very little of the injected CO_2 migrates out of the injection zone during the simulations. Figure 4 shows the extent of upward CO_2 migration into the caprock for a location immediately adjacent to the injection well.

For compositional models a rectangular simulation area was divided into polygonal cells that increase in size away from the center of the model, which is the location of the injection well. The lateral boundaries of the model were set to different constant-pressure values, which introduces a regional gradient and flow direction to fluids within the model. This in turn allows simulation of post-injection conditions after the end of CO_2 injection.

Figure 4. Gas saturation (vertical axis) as a fraction of the pore space versus vertical distance (horizontal axis, meters) for injection into the Reagan Sandstone. The model injection rate is 4.1 x 10^5 metric tons per year over 30 years. The base and top of the Reagan are at 80 and 111 meters, respectively. The model predicts significant downward migration of CO_2 into the Bonneterre and Lamotte formations, but very limited upward migration into the overlying caprock (Davis Formation).



For compositional models, CO_2 injection again was 30 years, followed by a 1000-year post-injection period, during which the CO_2 plume migrates in the direction of the pressure gradient while diluting due to diffusion, dispersion, and residual trapping. For compositional models with high regional gradients, the achievable injection rates are lower than those of the radial models (Table 8) due to distortion of the flow field around the well. Figures 5 and 6 show cross-sectional views of gas saturation near the injection well after the end of 30 years of injection and then a 1000-year post-injection period. The dissolved gas concentrations are much lower after 1000 years (note that the color scale is specific to the individual simulation). Also, vertical CO2 migration has only reached about half way through the caprock.

Figure 5. Compositional simulation for the Reagan Sandstone after 30 years injection at 2.1 x 10^5 metric tons per year. The regional pressure gradient is 9.8 Pa per meter.

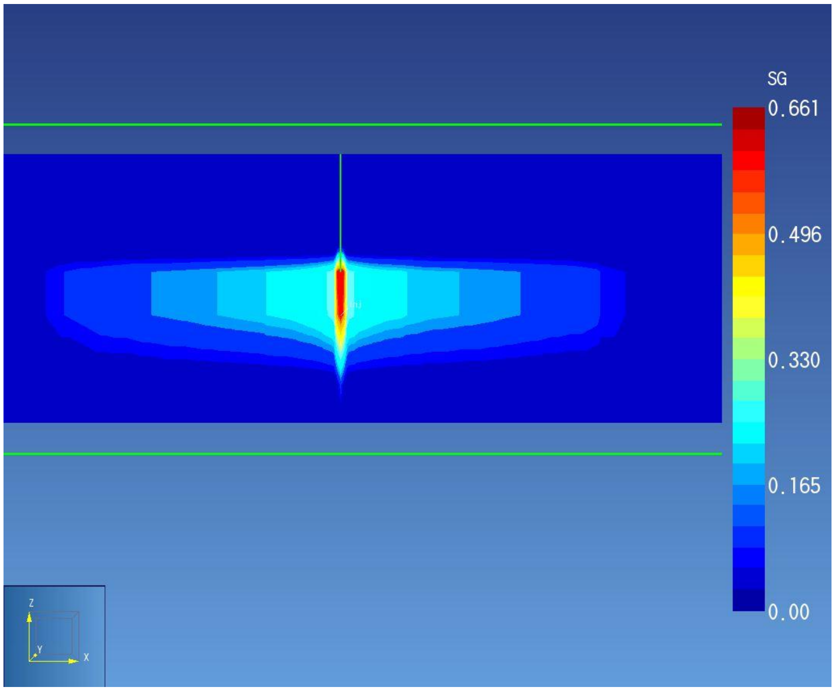
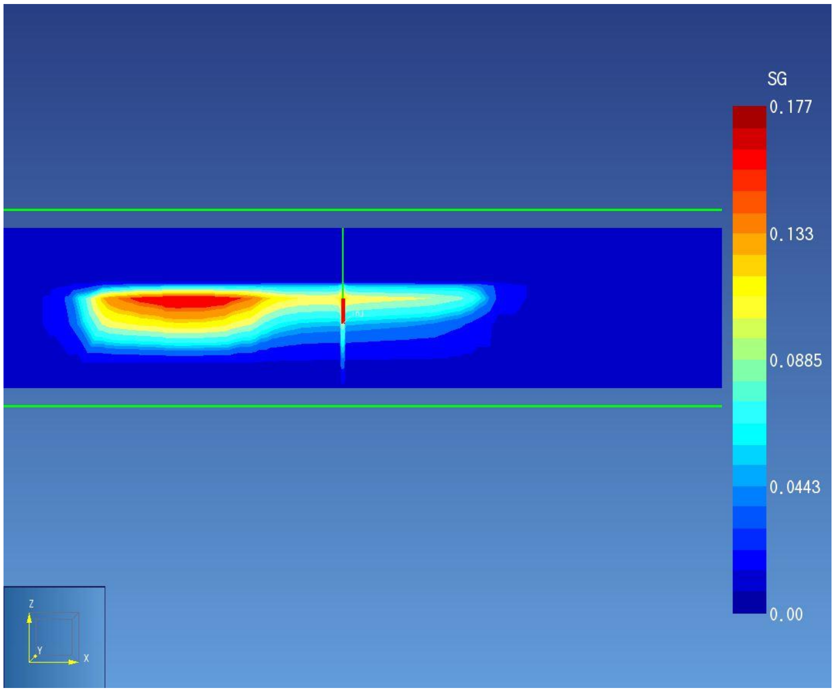


Figure 6. Compositional simulation for the Reagan Sandstone 1000 years after the end of injection. Parameters are the same as in Figure 5. The plume has migrated approximately 1500 meters to the left, and remains confined below the upper half of the caprock.



Task 3.0 Instrumentation and Monitoring.

Tables 9 and 10 show values for five data sets from locations where both pore-water chemistry and mineralogy, determined from cores, have been measured for the St. Francois aquifer (or closely related unit) within the same county. In two cases (Atchison and Holt Counties) proxy measurements from overlying strata were used for the pore-fluid chemistry. Four of the locations have highly saline pore water and at three of these the total dissolved solids concentration exceeds 10,000 mg/L, meeting requirements for CO_2 injection. The aquifer mineralogy is dominated by quartz, with minor feldspars, but importantly, all the sites included at least some glauconite and iron oxide material, which potentially can supply Fe^{+2} to react with sequestered CO_2 and precipitate the carbonate mineral siderite (Fe_2CO_3) as a solid phase. Various clay minerals are also present in low concentrations which may also provide di- or tri-valent cations to help precipitate various carbonate minerals.

Table 9. Water chemistry within the Lamotte Sandstone for several counties in Missouri. Dashes indicate that the specific parameter was not available. Values for Lawarence County (adjacent to Greene County) are listed to show the consistency in nearby areas. Values for Atchison and Holt Counties are proxy measurements taken from overlying strata.

	Northwest MO		Northeast MO		Southwest MO	
County	Atchison	Holt	Ralls	Lincoln	Greene	Lawrence
# of wells	1	1	1	1	1	1
Depth (m)	477	443	672	759	667	520
Ca^{+2}	17.9	168.9	632.4	1401	22.7	32.9
Mg^{+2}	31.8	77.9	253.9	320.0	8.3	15.3
Na^{+}	3615	4620	4032	7738	12.6	4.3
K^{+}	86.0	110.0	103.0	192.0	3.3	1.7
Fe^{+2}	0.5	0.5	0.3	0.25	0.83	---
Al^{+3}	0.4	0.4	0.7	0.7	----	---
Silica	2.6	6.4	8.0	8.0	4.51	---
Cl^{-}	5,491	8,132	6,667	14,940	2.64	---
SO_4^{-2}	690	11.9	1044	564.6	12.7	13.30
HCO_3^{-}	46.8	257.9	297.6	66.5	81.7	131.0
TDS	10,237	15,414	15,385	29,251	226	148

Table 10. Estimated percentages of major minerals in the Lamotte Sandtsone and their reactive surface area. Area is in cm^2 per gram (in parenthesis), estimated from Nondorf (2010). Feldspars include albite and potassium feldspar; clays include montmorillonite, kaolinite and ilite; micas include muscovite and chlorite.

Depth (m) County	Quartz (20.0)	Feldspars (101.0)	Clays (1012.0)	Glauconite (1012.0)	Micas (1012.0)	Iron oxides (1012.0)
Atchison County						
1146	92.0	4.0	2.0	1.0	0.5	0.5
1162	95.0	3.1	1.2	0.2	0.1	0.3
Holt County						
1058	92.0	3.5	2.0	1.0	0.5	1.0
1067	91.0	4.5	2.0	2.0	0.5	1.0
1082	92.5	4.0	2.0	0.5	0.2	0.8
Ralls County						
576	95.0	2.0	1.0	0.5	0.5	1.0
588	93.0	3.0	0.5	1.0	0.4	2.1
610	92.0	3.5	1.0	1.0	0.0	3.0
Lincoln County						
648	92.0	3.0	0.5	1.0	0.5	3.0
Greene County						
609	90.6	0.7	2.7	2.3	1.7	1.7

Simulation of injection into the St. Francois aquifer was accomplished by setting the CO_2 fugacity to a (conservative) value 20% higher than the initial CO_2 fugacity at the top of the Lamotte Sandstone. Rates of mineral dissolution and precipitation were simulated using rate constants from the database of Palandri and Kharaka (2004). The fugacity value was held constant for a ten-year period, simulating a short-term 10-year injection, and then allowed to vary for an indefinite post-injection period, but long enough for the pore water to reach equilibrium with the specified mineralogy and pore-fluid chemistry.

The amount of CO_2 (in grams per kilogram of pore water) sequestered in various aqueous and solid phases is shown for the 10-year injection period and the post-injection period in Tables 11 and 12, respectively. Figures 7 and 8 depict some of the more-important chemical changes occurring within the system. Upon injection, pH decreases rapidly due to CO_2 dissolution and $HCO3^-$ formation. Due to the lower pH, glauconite and the clay minerals quickly begin to dissolve, releasing Fe^{+2} and Al^{+3} while the iron-oxide minerals dissolve more slowly, releasing additional Fe^{+2}.

Both siderite and dawsonite are predicted to precipitate during the injection period, mostly within the first five years. Thereafter, precipitation slows as the available cations, from both the original pore water and from dissolution, are mostly depleted. Some precipitation of these two minerals continues at a slow rate for more than 1000 years as additional cations become available. At the SWPP site an additional carbonate mineral, magnesite, also slowly precipitates during the post-injection period.

Under the conditions simulated here, approximately 2-3 g of CO_2 are precipitated per kg of pore fluid by the time of equilibrium. As the CO_2 fugacity decreases during the post-injection phase the dissolved mass of CO_2, expressed as various complexed aqueous species, decreases slightly compared to the injection period. Nevertheless, over the entire plume large amounts of CO_2 would be sequestered in a non-gas phase, mostly as dissolved species, but some also as a precipitated carbonate mineral.

Table 11. Estimated amount of CO_2 sequestered during a 10-year injection period. Amounts are in grams per kg of free water.

	Northwest Missouri		Northeast Missouri		Southwest Missouri
County	Atchison	Holt	Ralls	Lincoln	Greene
Solubility Trapping					
CO_2(aq)	75.6	72.5	56.5	55.1	83.5
$HCO3^-$	0.81	0.61	0.88	0.66	6.1
NaHCO3	0.07	0.06	0.07	0.09	0.01
FeHCO3+	0.01	0.02	0.01	0.01	0.02
CaHCO3+	<0.01	0.01	0.06	0.08	0.86
MgHCO3+	<0.01	0.01	0.02	0.02	0.08
Total Solubility Trapping	73.5	73.2	57.6	56.0	85.4
Mineral Trapping					
Dawsonite, $NaAlCO_3(OH)_2$	0.3	1.1	0.2	0.5	< 0.01
Siderite, $FeCO_3$	1.8	2.3	2.2	2.1	11.6
Total Mineral Trapping	2.1	3.3	2.4	2.6	11.6
Total	75.6	76.5	60.0	58.6	97.0

Table 12. Estimated amount of CO_2 sequestered during post injection (cessation of injection to equilibrium and time to reach equilibrium. Amounts are in grams per kg of free water.

	Northwest Missouri		Northeast Missouri		Southwest MO
County	Atchison	Holt	Ralls	Lincoln	Greene
Solubility Trapping					
CO_2(aq)	67.2	65.0	47.6	55.1	70.2
$HCO3^-$	0.80	0.5	0.8	0.66	7.1
$CaHCO_3^+$	<0.01	0.01	0.1	0.08	0.17
MgHCO3+	<0.01	0.01	0.02	0.02	0.42
$FeHCO_3^-$	0.01	0.02	0.01	0.01	0.01
NaHCO3	0.07	0.04	0.06	0.09	0.01
Total Solubility Trapping	68.1	65.6	48.6	56.0	77.9
Equilibrium (years)	60	40	85	75	130
Mineral Trapping					
Magnesite, $MgCO_3$	ND	ND	ND	ND	6.5
Siderite, $FeCO_3$	2.0	3.1	2.5	2.1	11.9
Dawsonite, $NaAlCO_3(OH)_2$	2.9	2.6	3.0	0.51	ND
Total Mineral Trapping	4.9	5.6	5.5	2.6	18.4
Equilibrium (years)	1200	1200	500	500	2000
Total	73.0	71.1	54.1	58.6	96.3

Figure 7. Concentration of some chemical species (molal) and pH as a function of time during the injection period for (a) Atchison County in northwest MO and (b) Ralls County in northeast MO. Note the increase in Fe^{+2}.

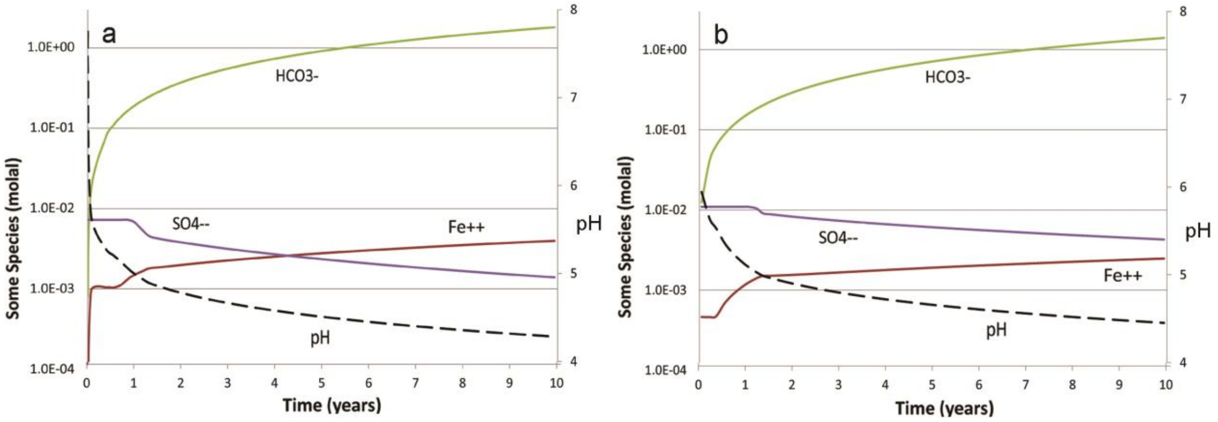
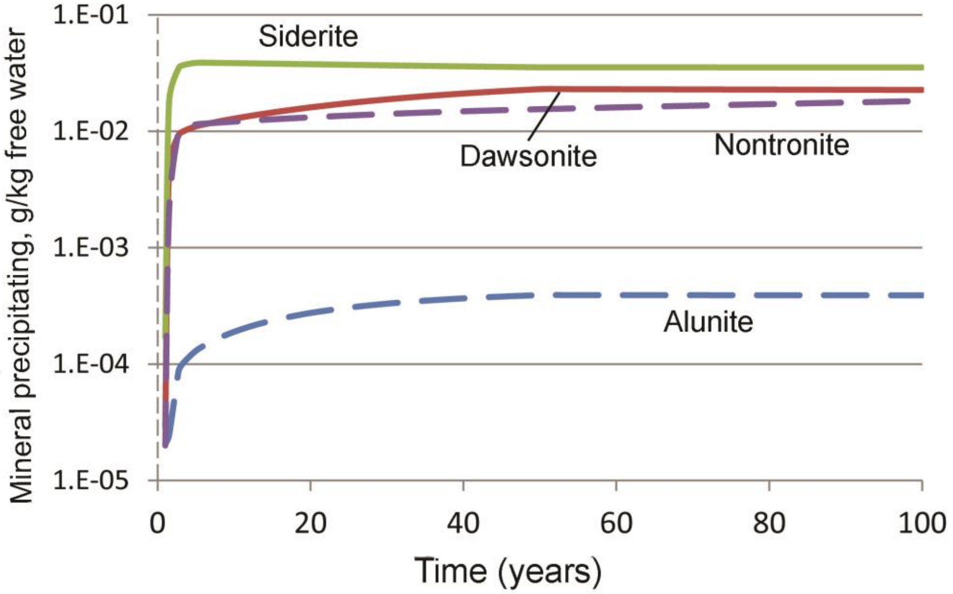


Figure 8. Mineral trapping of CO_2 by siderite and dawsonite at the northwest MO (Atchison County) site during post-injection. Alunite and nontronite also precipitate, but these do not sequester CO_2.



Task 4.0 Construction of a GIS Data Base of Pore-Fluid Chemistry within Missouri Aquifers.

Historically, water-quality and hydrochemical facies have been reported to be similar throughout the central geographic extent of the aquifer. In this study, slight lateral variations in major anions were found with some areas having a slightly higher chloride (Cl^-) content and other areas having a slightly higher sulfate ($SO4^{-2}$) content. The only possible vertical variation identified between the upper and lower portions of the Ozark aquifer was that fluorine content differed in some small areas where a few wells could be identified as being discretely within the lower portions or discretely within the upper portions of the aquifer. Unfortunately, there were not enough discretely screened wells to allow full identification of this possible differentiating factor. If carbon sequestration projects continue in Missouri, expanding upon the existing database and clustering the geochemical data into a factor analysis or principal component analysis might offer more insight into possible vertical geochemical variability within the Ozark aquifer.

Figures 9 through 12 display the variability across the Ozark plateaus region of selected major constituents within the Ozark Aquifer. Figures 13 and 14 show the preliminary results of mapping eigenvectors, which are essentially derivatives of the dataset related to the rate of change within the data. The eigenvectors for monovalent and divalent ions were mapped in an attempt to investigate the potential utility of factor analysis or principal component analysis as a means of differentiating geochemical conditions within the Ozark aquifer. One can see from the increased variability in color gradations that the eigenvectors do display more variation laterally within the Ozark aquifer than the major constituents each show individually (as noted in Figures 9-12). Given this lateral variation, it seems reasonable to anticipate that additional data and data processing might allow similar variability to be determined vertically within the Ozark aquifer. If vertical geochemical changes can be identified within the Ozark aquifer, then more detailed chemistry of the lower Ozark aquifer – which would be the area most susceptible to first show impacts of carbon dioxide leakage from injection into the underlying St. Francois aquifer – might be possible. Until such additional data and determinations can be made, the existing ranges of known major species will have to suffice as the “background” dataset of pre-injection, un-impacted conditions within the Ozark aquifer.

Figure 9. Calcium ion concentration within the Ozark aquifer, across the Ozark Plateau region.

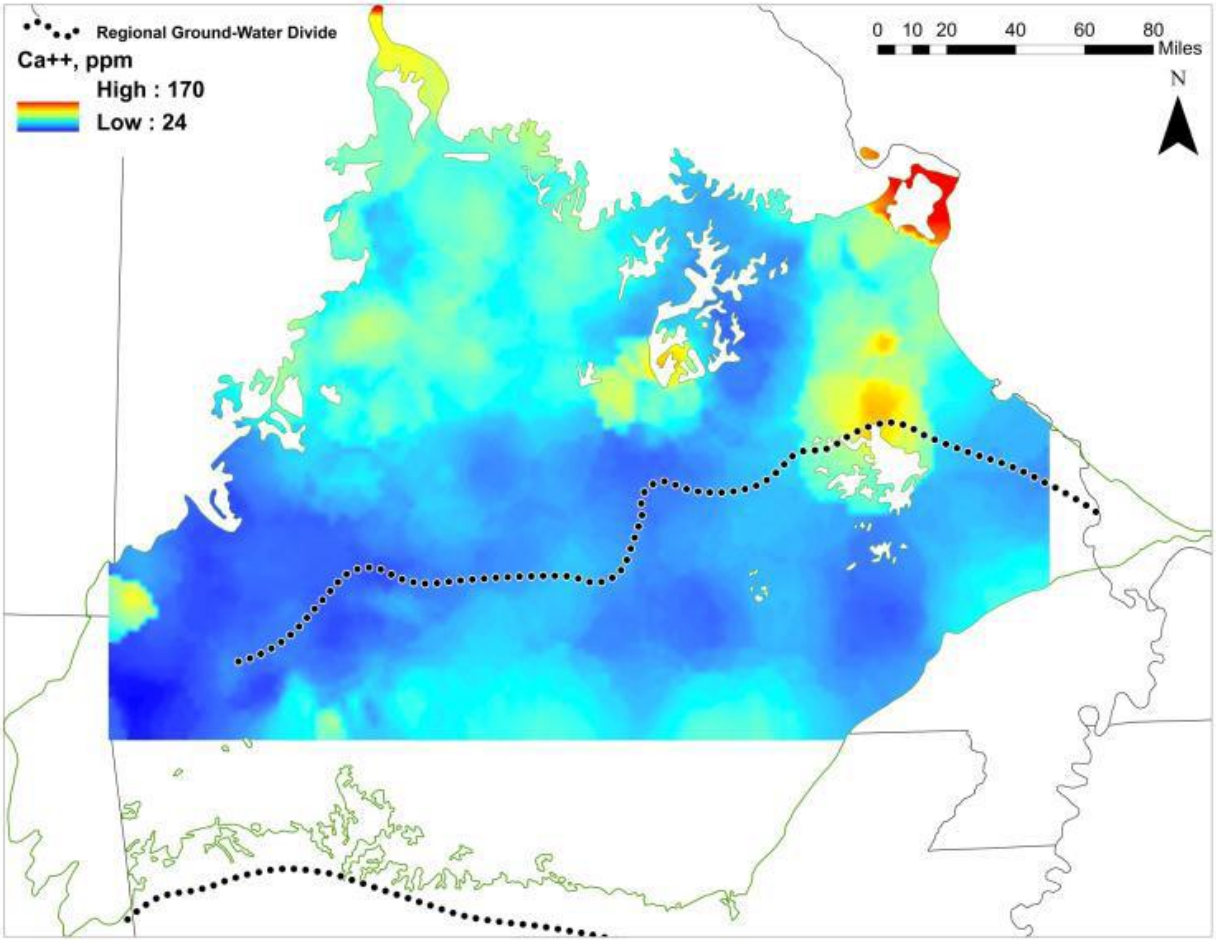


Figure 10. Magneisum ion concentration within the Ozark aquifer, across the Ozark Plateau region.

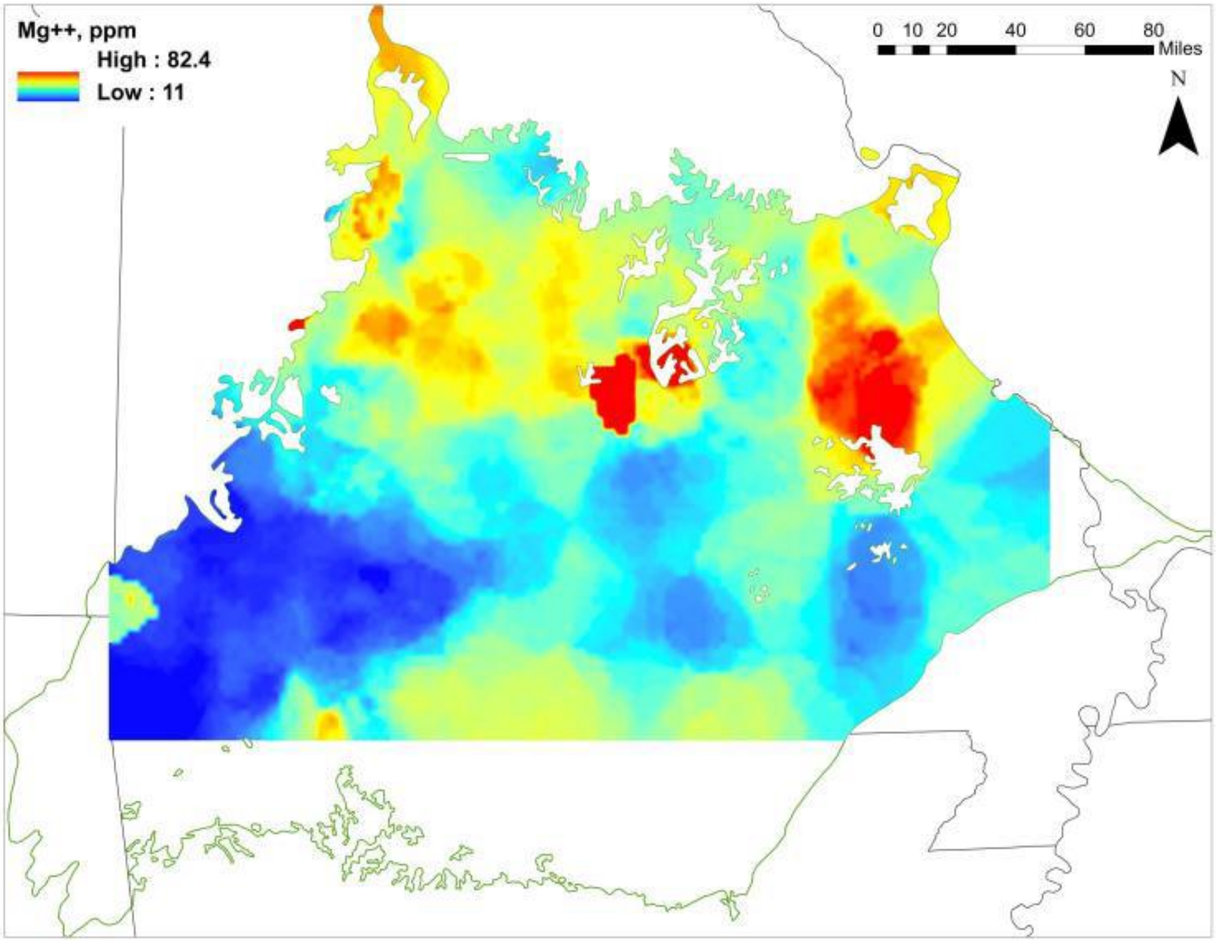


Figure 11. Sulfate species concentration within the Ozark aquifer, across the Ozark Plateau region.

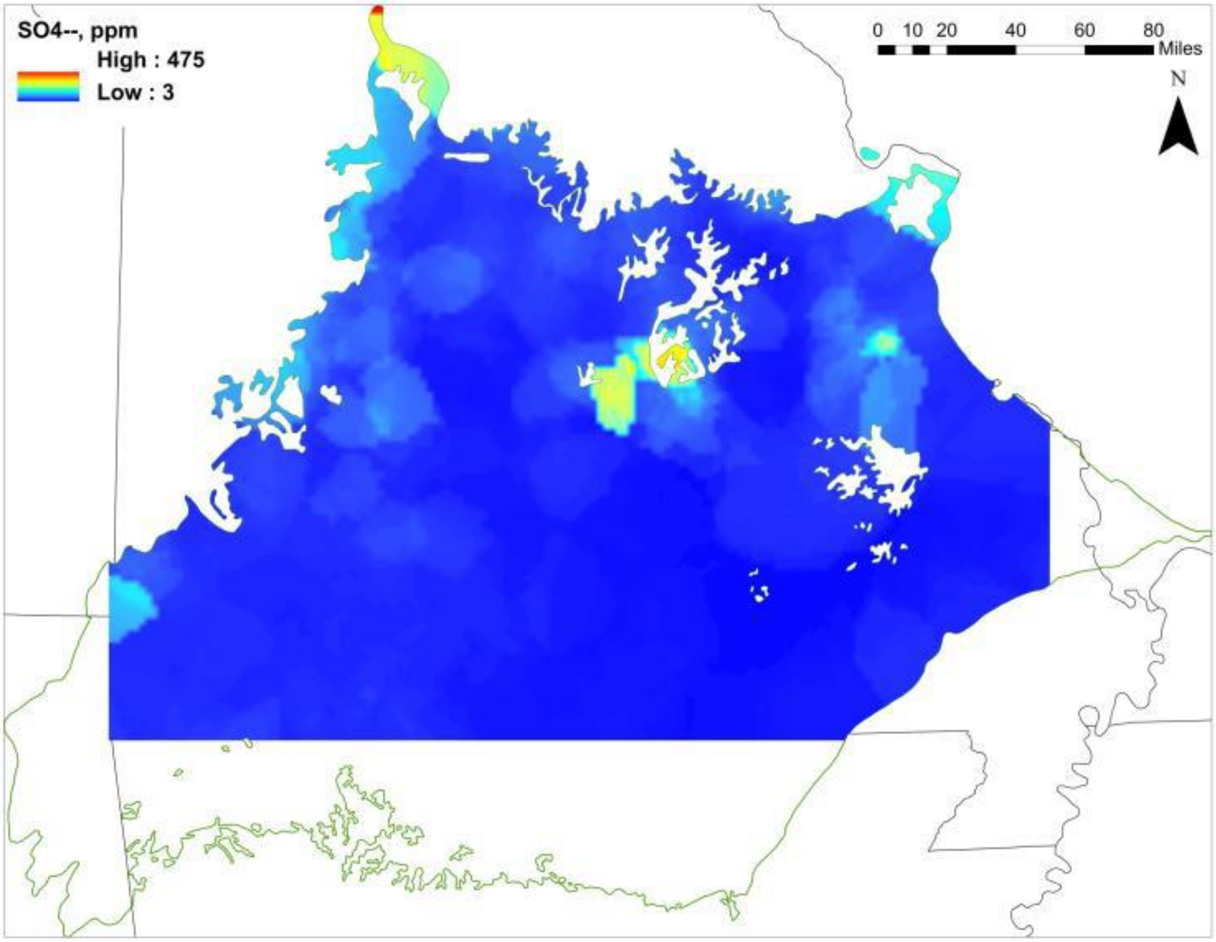


Figure 12. Chloride ion concentration within the Ozark aquifer, across the Ozark Plateau region.

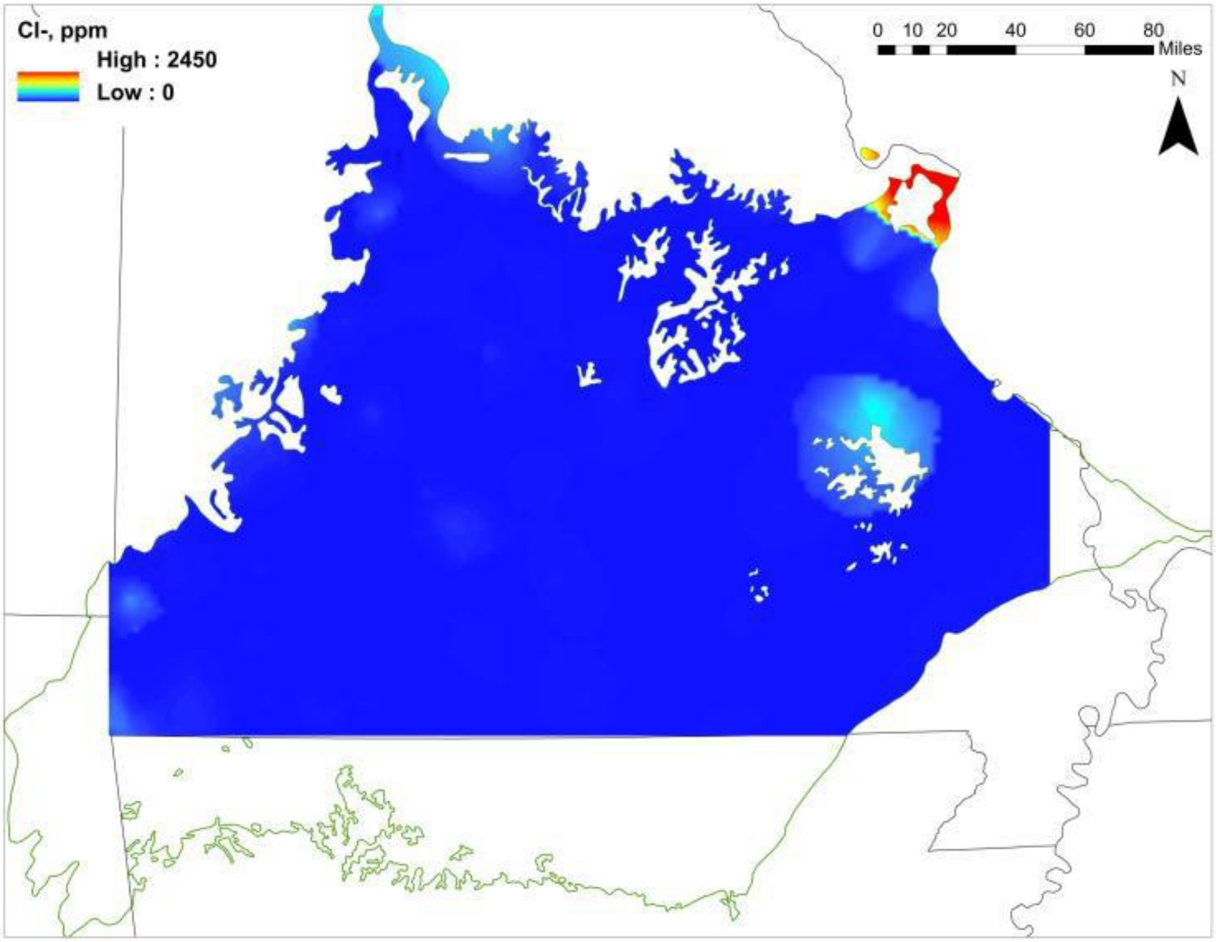


Figure 13. Monovalent ion group eigenvector score within the Ozark aquifer, across the Ozark Plateau Region.

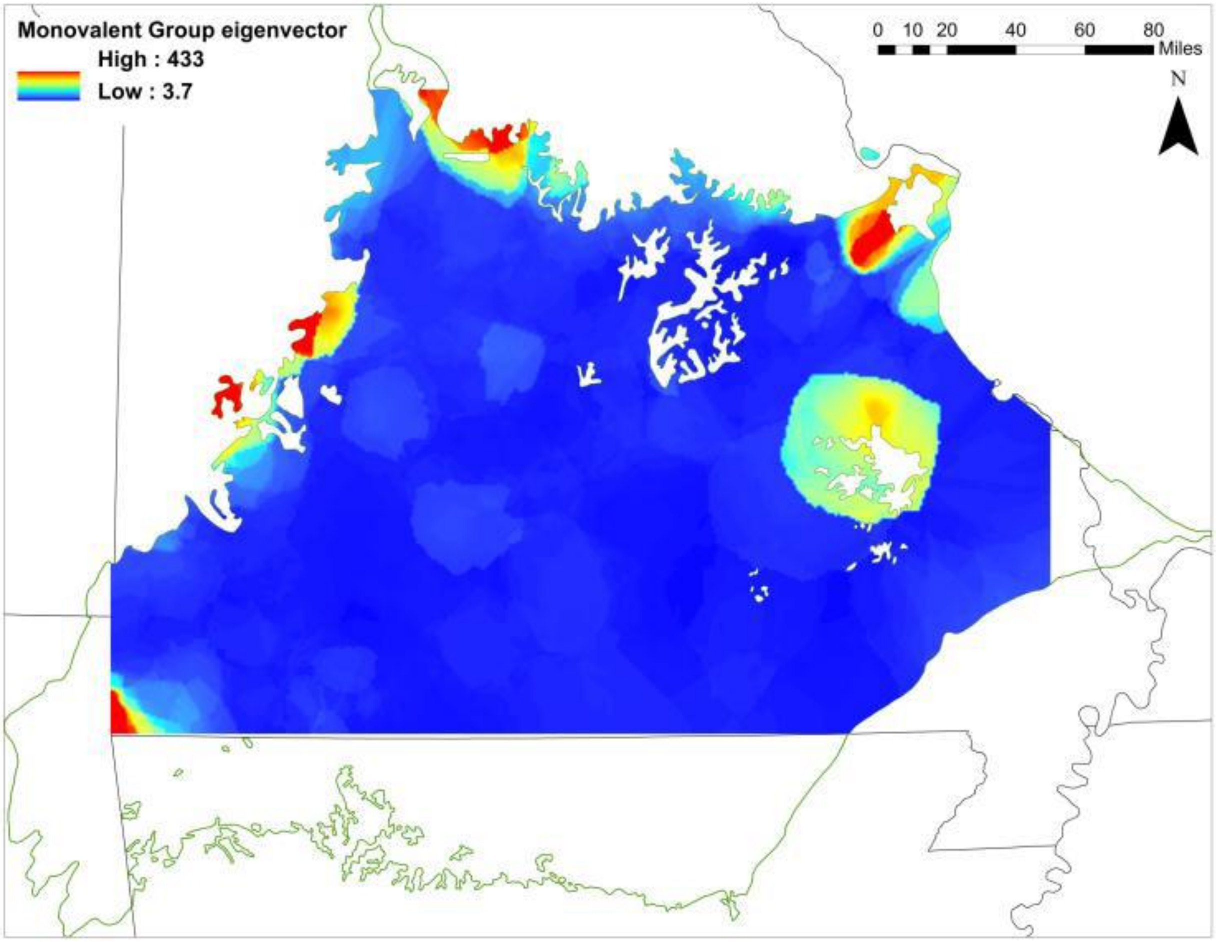
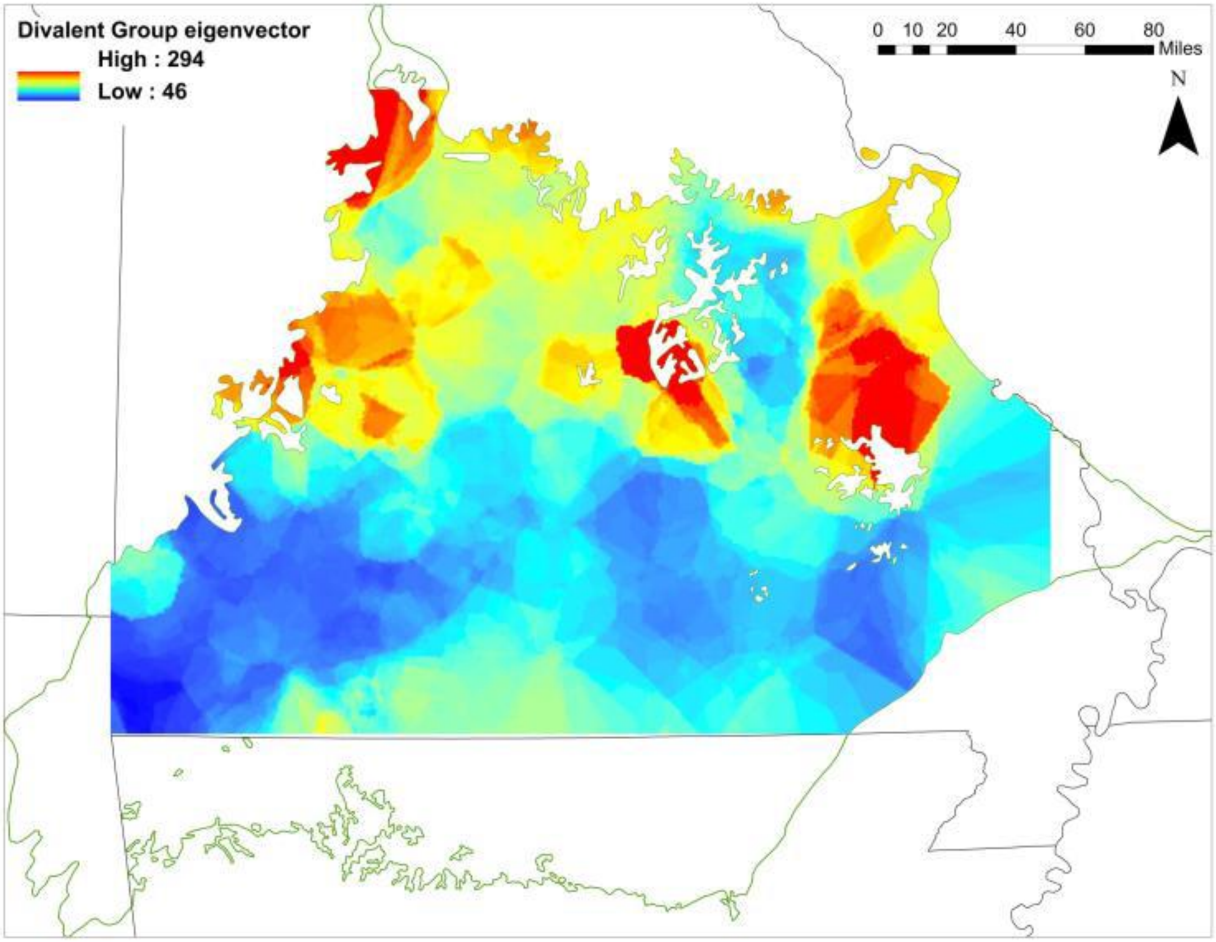


Figure 14. Divalent ion group eigenvector score within the Ozark aquifer, across the Ozark Plateau Region.



Future work can be conducted using the existing database and expanding the database to include additional areas in Missouri. It appears likely that clustering functions or principal component analyses or similar statistical methods may allow greater differentiation of groundwater chemistry of the Ozark aquifer as additional data become available.

Conclusions

Simulation of CO_2 injection into the St. Francois aquifer system at the Greene County, Missouri SWPP site indicates that this stratigraphic unit is a viable candidate for CO_2 sequestration where the pore fluids are saline. Sandstone within this unit is capable of sustaining relatively high injection rates at low injection pressure. The caprock above this aquifer includes strata with very low permeability and simulations also predict that these layers would prevent injected CO2 from reaching overlying aquifers for >1000 years.

The mineral composition of the aquifer would also aid in the sequestering CO_2 over geologic time scales. Geochemical models predict that accessory minerals within the aquifer would react rapidly with injected CO_2 to release cations which would then precipitate and remove CO_2 as various carbonate minerals.

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