

SUPPLEMENTAL SECTION COVER PAGE

TITLE: Effect of Dissolved CO₂ on a Shallow Groundwater System—A Controlled Release Field Experiment

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SUMMARY

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SUPPORTING INFORMATION

SITE BACKGROUND INFORMATION

Mississippi Power Company's Victor J. Daniel Power Plant (Plant Daniel) is located approximately 10 miles north of the city of Pascagoula, in Jackson County, Mississippi. The plant has 4 generating units, including two coal-fired, sub-critical drum type units and two gas-fired combined cycle units that bring the plant's total generation capacity to over 2,000 megawatts. The field site is located just to the North of the power plant within the confines of the plant property in a flat lying area. The site is located in Sections 11 of Township 6 South, Range 6 West of Jackson County, Mississippi.

The site was previously used by the Southeast Regional Carbon Sequestration Partnership (SECARB) for a small-scale CO₂ injection pilot test sponsored by Southern Company Services and the U.S. Department of Energy. The phase II pilot test involved injecting more than 2,722 metric tons of CO₂ into the Lower Tuscaloosa Sandstone at a depth ranging from 2,597 to 2,658 m below ground level. The SECARB wells have been temporarily plugged and are not being used by for the shallow CO₂ impact study, but the wells for both studies are co-located.

Regional Setting

The site is located in the Mississippi-Alabama Gulf Coast physiographic province. Two physiographic provinces make up this area: the Piney Belt province in upland regions in the northeastern and northwestern corners of the county and the Coastal Zone province in central Jackson County lowlands where Plant Daniel is located. The Pascagoula River drainage basin collects most surface water in the central portion of Jackson County which flows into Pascagoula Bay and into the Gulf of Mexico. Drainage in the eastern portion of county along the Alabama border is via the Escatawpa River which also flows into Pascagoula Bay. The extreme western portion of the county is drained by various coastal streams which empty into Biloxi Bay. Surface drainage is characterized by dendritic patterns in the upland regions and by meandering streams and extensive floodplain development in the lowland areas.

Groundwater Hydrogeology

Jackson County is directly underlain by Pliocene and Miocene-age freshwater aquifers (also referred to as the “Sand and Gravel Aquifer” in the U.S. Geological Survey (USGS) Groundwater Atlas of the United States). Freshwater, defined as <1,000 mg/l total dissolved solids (TDS), occurs down to a depth of about 366 m in the eastern part of the county and to a depth of nearly 610 m in the southwestern corner of the county. Water with less than 10,000 TDS, defined by the U.S. Environmental Protection Agency (EPA) in waste injection regulations as a protected Underground Source of Drinking Water (USDW), occurs at depths shallower than 488 m in the northeast corner of the county and depths of over 853 m in the southwest corner of the county. The base of the lowermost USDW at the Plant Daniel site occurs at a depth of approximately 670 m below mean sea level.

Local Freshwater Hydrogeology

The USGS conducted a survey of 150 groundwater wells in Jackson County and found that freshwater is drawn from four major geologic units, the Citronelle, Graham Ferry, Pascagoula, and undifferentiated Miocene-age deposits. The shallowest freshwater aquifer in Jackson County is in the Citronelle Formation, a Pliocene-age sand which averages about 30 m in thickness and is overlain by a thin cover of Quaternary alluvium. The Citronelle outcrops in high elevation areas in Jackson County and in George County directly to the north and is an unconfined aquifer with meteoric recharge. Below the Citronelle is the approximately 30 m thick Graham Ferry Formation sand and clay aquifer which is heavily used as a freshwater source in Jackson, Harrison, and Hancock Counties which occurs at 21–183 m depth (average of 107 m). The test interval used for carbonated groundwater injection during this experiment is located in the upper section of the Graham Ferry Formation (Figure S1). Below the Graham Ferry Formation lies the freshwater Miocene-age aquifer system which is the deepest freshwater aquifer in Jackson County. The Miocene units range in thickness from 610 m in northern Jackson County to over 975 m thick along the coastline with about 305 m of net sand in the Pascagoula, Hattiesburg, and Catahoula Formations. The fresh water aquifer occurs at 21–427 m depth (average of

274 m) in Jackson County. The system dips to the south at about 5.7–19 m/km becoming steeper towards the coast. Only up-dip portions of the system contain freshwater and the system is a major freshwater supply along the Gulf Coast. Increasingly saline reservoirs exist in the down-dip, deep portions of these units.

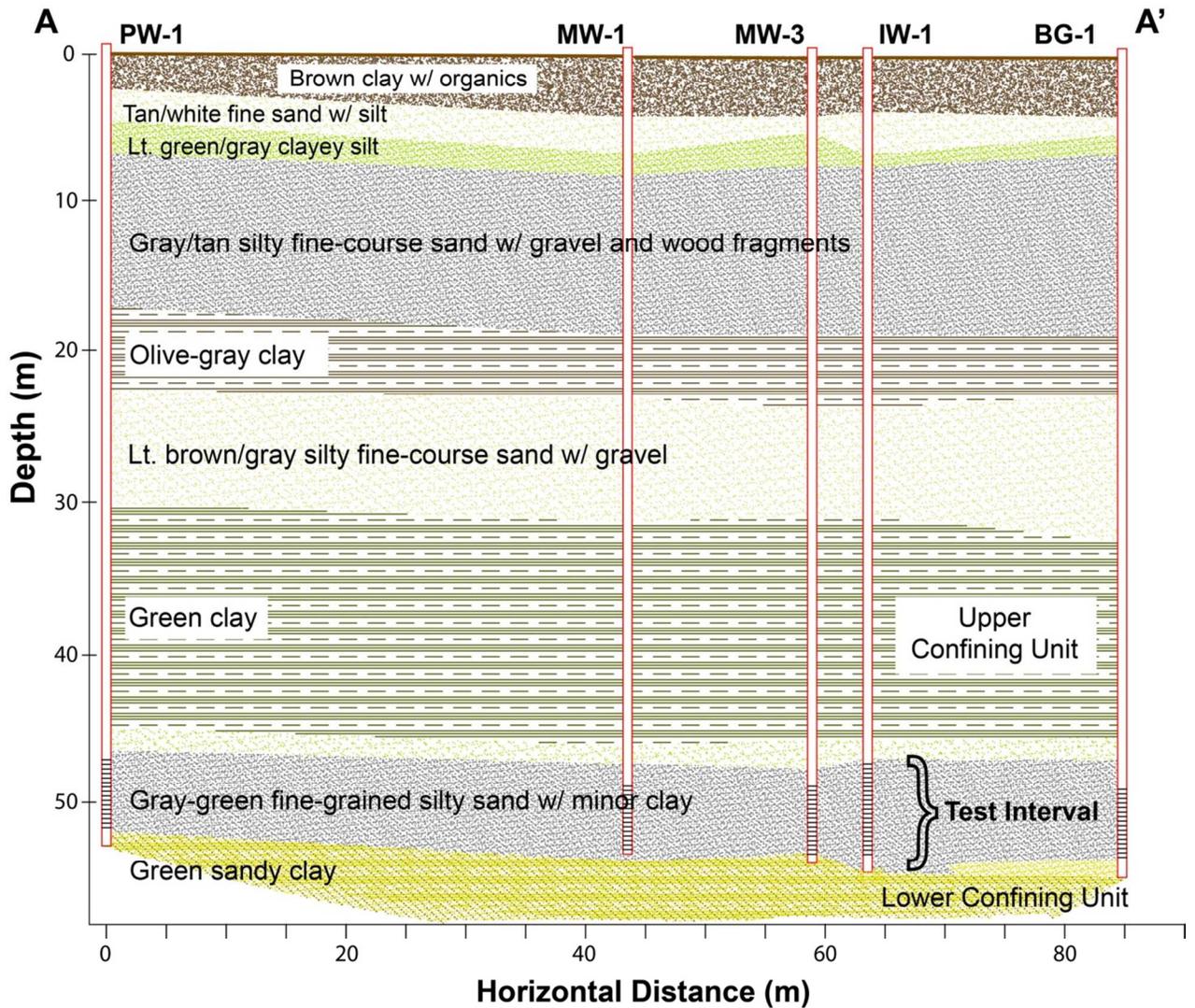


Figure S1. West (A) to East (A') section across the test site showing unconsolidated sediment lithology and the test interval where groundwater was pumped from PW-1, carbonated at land surface and then injected back into injection well IW-1.

Local Deep Hydrogeology

Beneath the Miocene-age aquifer system in Jackson County, all reservoirs contain > 10,000 mg/L, high-salinity brines. The sandstone sections of the Vicksburg Groups contain reservoirs of varying quality which are known as the Oligocene-age aquifer system. Below the Oligocene-age aquifer system are the Eocene-age Claiborne and Wilcox reservoirs. The Wilcox is a prolific aquifer with freshwater beginning about 97 km updip to the north of Jackson County, in central Mississippi and Alabama. In addition, while the Wilcox occurs at a depth where CO₂ is in its supercritical phase (>762 m) and the brine portion of the reservoir maybe suitably distant from any freshwater sections of the reservoir, the lack of a confining unit traceable over a large area eliminates it from consideration as a candidate for CO₂ storage.

ARGON HEADSPACE ANALYSES AND RESULTS

Methods

Measurement of dissolved argon from groundwater samples is accomplished through headspace equilibration techniques. Argon gas concentrations are measured in the headspace of sample vials, and known Henry's Law coefficients and mass balance relationships are applied to calculate the concentration of dissolved argon in collected groundwater samples.

Sample Collection and Extraction

Groundwater samples were collected into 0.95 centimeter (cm) O.D. copper tubes sealed either with Swagelock® valves or refrigeration crimping clamps. Samples were collected at a back pressure of approximately 1.4 bar to ensure that argon remained dissolved in the groundwater. Back pressure prevents gas bubble formation in the samples tubes during sampling which would introduce significant error in the dissolved argon analysis.

Samples of water were extracted from the copper tubes into evacuated headspace vials. Figure S2 shows the extraction system. This system was designed to prevent degassing of water samples and to minimize atmospheric gas contamination during the extraction. Prior to extraction, 20 ml headspace vials initially sealed with teflon-lined septa were evacuated using a glass vacuum line. Subsequent improvements to the extraction technique employed Butyl Rubber septa manufactured by Geo-Microbial Technologies, Inc., and these stoppers significantly lowered blank corrections for the samples. Water was transferred from the copper tubing to the headspace vials by orienting the copper tubes vertically and attaching a water head (separatory funnel) to the top of the tube to facilitate water extraction out of the bottom of the tube without forming a gas head. The manifold at the bottom of the copper tubes were evacuated by creating a vacuum with the attached syringe. For extraction, the valves were opened, the syringe was used to pull any air contamination away and the evacuated vial was pierced with the syringe. Approximately 7 ml of water was injected into the pre-weighed headspace vial. It was necessary to quickly add helium gas to the headspace vials to maintain a constant atmospheric pressure, without losing any argon gas that may have evolved during the water extraction. This was accomplished by injecting helium into the headspace vial with a two-holed needle.

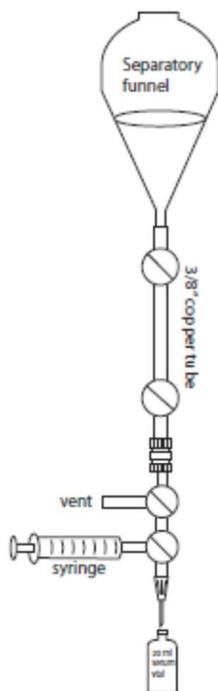


Figure S2. Sample extraction system.

One hole was connected to a research-grade source of helium; the second hole was connected to vent tubing that was connected to a water-filled beaker. As soon as the vent lining showed signs that the vial was equilibrated, the helium source was removed. Following this procedure the vials were weighed, the volume of water and headspace was calculated, and the vials were stored upside down at a constant temperature overnight. Two headspace vials were collected from each sample tube, but only the first vial was used for argon analysis.

Argon Analysis

Concentrations of argon in water samples were calculated using mass balance relationships and known Henry's law coefficients. Samples were equilibrated at 25°C. Calibrated mass of argon was measured in the headspace using gas chromatography mass spectrometry (GCMS). Briefly, 2 ml aliquots of headspace gas were injected into an Agilent 6890 gas chromatograph. The injection port was heated to 250°C with a 5:1 split. A Restek (RT-MSieve 5Å) chromatography column with a helium flow rate of 1.5 ml/min was used to separate nitrogen from oxygen and argon. The oven was initially heated

to 50°C for 1 minute and ramped to 300°C at a temperature ramp of 25°C/min. Although this configuration does not separate argon and oxygen, selective ion scanning mass spectrometry was used for separate argon calibrations. An argon calibration curve was formed using GCMS measurements of calibrated argon gas standards. Three calibrated standards and internal helium blank were used to form the calibration curve.

Headspace gas measurements of argon in the equilibrated water sample were used to calculate the concentration of dissolved argon in the water samples. This requires mass balance relationships and Henry's law coefficients. The headspace and aqueous volumes were calculated gravimetrically during sample loading. Temperature was recorded during equilibration. Headspace concentrations are initially recorded in micromoles argon/Liter headspace. A unitless Henry's Law coefficient of 3.43E-2 (mol/L in water divided by mol/L in gas at 25°C and 1 bar) is applied to calculate the concentration of dissolved argon in the equilibrated aqueous samples. Total argon in the groundwater sample was calculated using mass balance. That is, the headspace mass of argon was added to the aqueous mass of argon in the headspace vial to calculate the total groundwater concentration.

Argon Results

Argon concentrations in groundwater for the injection well (IW-1) and the nearest monitoring well (MW-3) are provided in Table S1. The concentrations reported for IW-1 are not the groundwater concentration of water pumped from the well, but rather the concentration of argon saturated groundwater injected into the well. These samples were collected at the surface in-line with the gas saturation apparatus. The MW-3 samples are downhole groundwater samples collected by pumping. Note that the baseline concentrations for the injection water and MW-3 match fairly well. Concentrations at MW-3 begin to deviate significantly from baseline on August 25, 2011.

Table S1. Argon concentration dissolved in groundwater.

Well	Date	Argon (μM)	Argon (ppm)	Note
IW-1	8/15/2011	56.0	2.2	Pre-argon saturation baseline
IW-1	8/15/2011	1721.8	68.7	argon injection
IW-1	8/16/2011	995.7	39.7	argon injection
IW-1	8/16/2011	2524.6	100.7	argon injection
IW-1	8/16/2011	823.7	32.9	argon injection
IW-1	8/17/2011	1177.1	47.0	argon injection
IW-1	8/17/2011	657.3	26.2	argon injection
IW-1	8/18/2011	339.4	13.5	argon injection
MW-3	8/9/2011	61.3	2.5	baseline
MW-3	8/15/2011	46.2	1.9	baseline
MW-3	8/17/2011	62.3	2.5	
MW-3	8/19/2011	78.4	3.1	
MW-3	8/21/2011	77.6	3.1	
MW-3	8/23/2011	82.4	3.3	
MW-3	8/25/2011	116.7	4.7	
MW-3	8/27/2011	159.7	6.4	
MW-3	8/29/2011	177.6	7.1	
MW-3	9/1/2011	53.1	2.1	
MW-3	10/21/2011	69.36	2.8	
MW-3	11/2/2011	44.7	1.8	

MW-3	11/9/2011	41.0	1.6	
MW-3	11/30/2011	70.5	2.8	
BG-1	9/7/2011	56.1	2.24	background

LIST OF CONSTITUENTS

Table S2. Groundwater samples were analyzed in the laboratory for the constituents identified in this table during all phases of the study (i.e., pre-injection baseline, during dissolved CO₂ injection and post-injection monitoring).

Category/ Analysis	Constituent(s)	Analytical Method
Major/Minor Cations	Al, Ba, Ca, Fe, K, Li, Mg, Mn Na, Si, Sr	SW846 6020A
Anions	Br, Cl, F, HCO ₃ , NO ₃ /NO ₂ , PO ₄ , SO ₄	EPA 300.1
Trace Elements	Ag, As, Be, Co, Cd, Cr, Cu, Hg, Mo, Ni, P, Pb, Sb, Se, Tl, Zn	SW846 6020A (Hg 7472, P by EPA 365.4)
Organic Carbon	Total/dissolved organic carbon, Organic acids (e.g., acetate, propionate, lactate)	SW846-9060/MCAWW 415.1 (for TOC), Ion chromatography/LC-MS for organics
Dissolved gases/volatile species	CH ₄ , H ₂ S, total dissolved sulfide (H ₂ S/HS ⁻), NH ₃	RSK 175, TDS with MCAWW 376.1, SM 4500-NH3 for solution
Field measurements		
General	pH, electrical conductivity, dissolved oxygen, ORP, turbidity/TDS, temperature	Field Probe (e.g. hydrolab or YSI sonde)
Alkalinity	Carbonate and bicarbonate alkalinity	Field alkalinity titration (and SM2320B)
Field, redox-sensitive	Fe ³⁺ /Fe ²⁺ ; Total dissolved sulfide (H ₂ S/HS ⁻)	Colorimetric ferrozine kit; Field kit using Methylene blue

GROUNDWATER MONITORING

Four groundwater monitoring wells were installed at the site for the purpose of collecting groundwater quality samples and making *in situ* measurements (pH, temperature, pressure and electrical conductance). Each well contained an air actuated, low-flow bladder pump that remained in the well during all phases of the project (pre-injection, injection and post-injection). A dedicated pump was installed in each well to minimize cross-contamination and disturbance of the groundwater redox conditions inadvertently caused by lowering pumps and instruments containing entrapped air into the wells. An innovative sampling device consisting of a flow-through cell containing an electrical conductivity, pH and temperature probe and a back pressure regulator were used to collect a pressurized (1.4 bar) groundwater sample. Groundwater was pumped through the discharge against the backpressure regulator to prevent exsolution of dissolved gases in the pump discharge line as the groundwater is pumped to the surface. Background groundwater samples were collected from the wells starting a minimum of 12 months (Table S3) prior to dissolve-CO₂ injection to capture seasonal variations in groundwater quality.

Table S3. Well installation dates and numbers of background sampling events performed per well.

Well	Installation Date	First Sample Date	# Total Events Prior to Argon Test	# Total Events Prior to CO₂ Test	# Events After CO₂ Test
MW-1	Feb 2010	Feb 2010	13	16	22
MW-2	Feb 2010	Feb 2010	13	16	26
MW-3	Aug 2010	Sep 2010	14	23	24
MW-4	Aug 2010	Sep 2010	10	13	5

FLOW AND GEOCHEMICAL MODELING

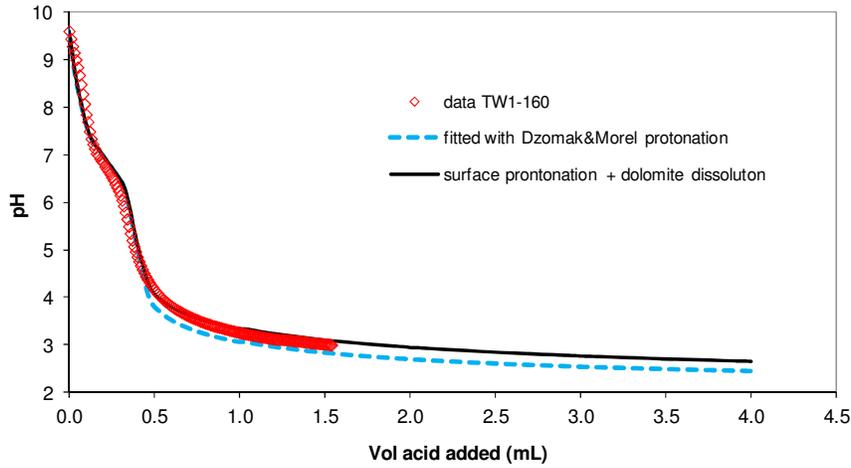


Figure S3. Sediment titration curve (symbols) with modeled data assuming surface protonation of Fe hydroxides with (solid line) and without (dashed line) the small amount of solid carbonates (0.006 vol%) assumed in the model.

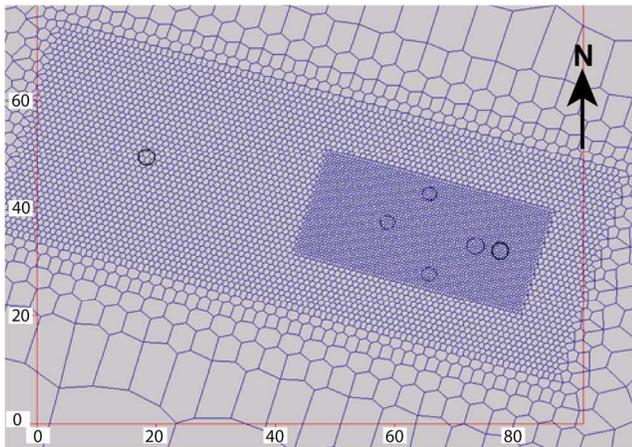


Figure S4. A close-up view of mesh at the area of interest, with coordinates in meters. The centers of the circles correspond to the positions of wells.

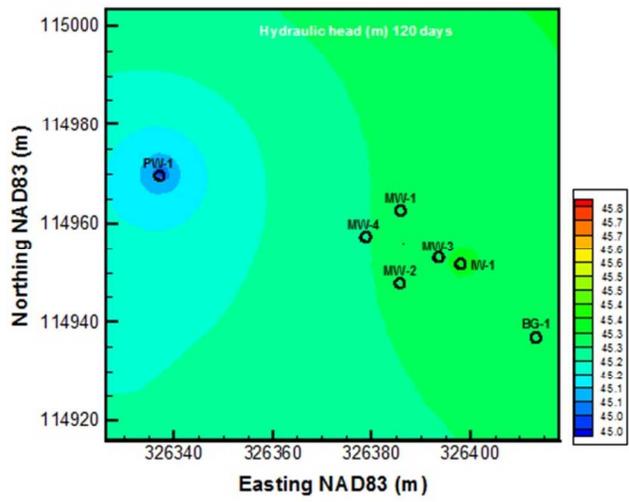


Figure S5. Computed spatial distribution of hydraulic head (m) after 120 days of pumping the sand unit.

Table S4. Compositions of initial and Injected Waters Used in the Model. The Units of Concentrations of Chemical Species is Molality Except for pH.

Species	Initial Water	Injected Water
pH	7.94	4.97
Al	4.45E-06	4.45E-06
Ba	4.07E-07	4.07E-07
Br	8.27E-07	8.27E-07
Ca	7.34E-05	7.34E-05
Cd	8.45E-10	8.45E-10
Cl	7.31E-04	7.31E-04
Co	9.67E-09	9.67E-09
Cu	1.73E-08	1.73E-08
F	2.40E-05	2.40E-05
Fe(II)	4.00E-06	4.00E-06
C(+4)	6.22E-03	1.33E-01
P	3.18E-06	3.18E-06
K	7.10E-05	7.10E-05
Li	6.97E-06	6.97E-06
Mg	5.35E-05	5.35E-05
Mn	1.16E-06	1.16E-06
Mo	4.41E-08	4.41E-08

Species	Initial Water	Injected Water
Na	6.70E-03	6.70E-03
Ni	3.41E-08	3.41E-08
Pb	9.65E-10	9.65E-10
S(+6)	1.02E-05	1.02E-05
Sb	1.33E-08	1.33E-08
Si	1.75E-04	1.75E-04
Sr	1.13E-06	1.13E-06
Zn	2.14E-07	2.14E-07
S(-2)	3.70E-05	3.70E-05
Cr	4.81E-08	4.81E-08
Se	7.00E-09	7.00E-09
As	9.22E-09	9.22E-09
N(+5)	1.67E-04	1.67E-04
Acetic acid (aq)	5.31E-05	5.31E-05
Methane(aq)	9.87E-06	9.87E-06
Ethane(aq)	2.51E-05	2.51E-05
Hg	3.49E-10	3.49E-10
Fe(III)	3.46E-06	3.46E-06
O ₂ (aq) (computed from redox couple HS ⁻ /SO ₄ ⁻²)	1.08E-74	1.08E-74