

Kentucky Geological Survey
University of Kentucky, Lexington

Shallow Groundwater Monitoring Associated with the Deep Saline Reservoir CO₂ Storage Test in Hancock County, Kentucky

E. Glynn Beck

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Shallow Groundwater Monitoring Associated with the Deep Saline Reservoir CO₂ Storage Test in Hancock County, Kentucky

E. Glynn Beck

Abstract

A carbon dioxide injection test well was drilled in 2009 to a depth of 8,126 ft below ground surface in Hancock County, Kentucky. Six hundred ninety tons of CO₂ was successfully injected into Knox Group saline aquifers. Two domestic wells (MB and GB) and two domestic springs (CA and RC) were sampled to monitor any potential changes in groundwater quality associated with possible migration of CO₂ from deeper saline aquifers into shallow freshwater aquifers. The four sites were sampled for pH, bicarbonate, total dissolved solids, turbidity, anions, total dissolved metals, dissolved inorganic carbon, total CO₂, and delta carbon-13 of the dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$). Values of pH for the four sites ranged between 4.58 and 7.82 and were consistent over time at all sites. Bicarbonate, total CO₂, dissolved inorganic carbon, and TDS concentrations showed very little variation over time at all of the sites except at well MB. Although water chemistry at well MB varied during the monitoring period, $\delta^{13}\text{C}_{\text{DIC}}$ values suggested that injectate had not migrated into the shallow aquifer at that site. All groundwater geochemical data clearly indicate that injectate CO₂ had not migrated upward into the four monitored shallow aquifers before sampling was discontinued in August 2012.

Introduction

Reducing carbon dioxide emitted from coal-fired power plants and other industries has become an important goal and research topic both internationally (Metz and others, 2005) and in Kentucky. In 2007, the Kentucky General Assembly through House Bill 1 mandated that the Kentucky Geological Survey conduct research that "... shall include the drilling of deep wells in both coal fields (Illinois and Appalachian) in Kentucky, and performing the analysis necessary to estimate the potential for enhanced oil and gas recovery, enhanced coalbed methane recovery, or permanent storage of carbon dioxide" (Kentucky Legislature, 2007). A deep injection well, the KGS Marvin Blan No. 1, was drilled

in 2009 as part of this mandate to a depth of 8,126 ft (all depths below ground surface unless otherwise indicated) in Hancock County (Fig. 1). Successful geologic storage was demonstrated with the injection of 323 tons of CO₂ on August 18, 2009 (phase I) and an additional 367 tons of CO₂ on September 22, 2010 (phase II). During phases I and II, CO₂ was injected into Knox Group saline aquifers below a depth of 3,570 ft. The injection well was plugged and abandoned on October 18, 2011. Additional research findings related to this project are in Bowersox (2013) and Zhu and others (2013).

As mandated by U.S. Environmental Protection Agency underground injection control permit KYV0049, a groundwater monitoring well (MW1)

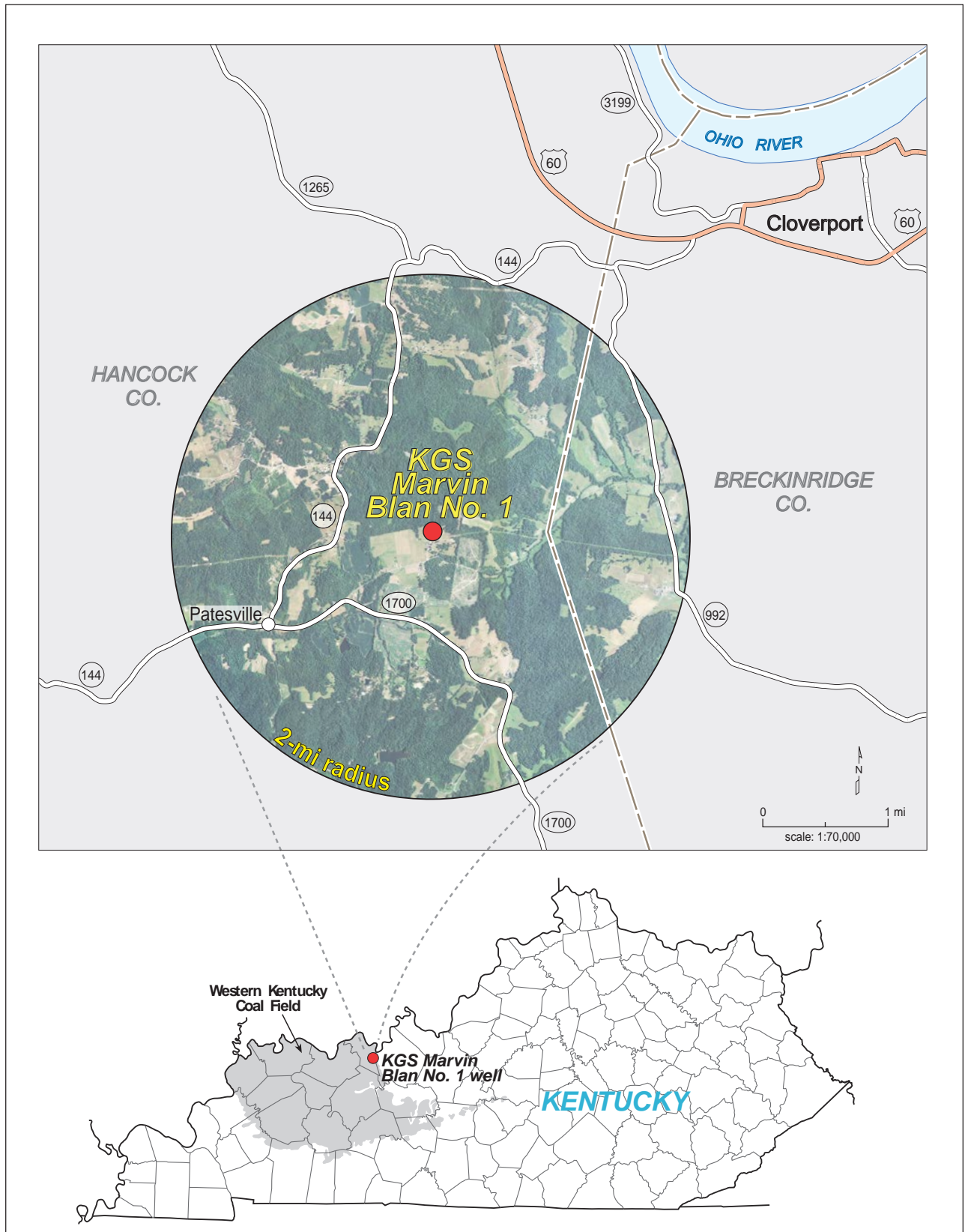


Figure 1. Location of the KGS Marvin Blan No. 1 injection well in the Western Kentucky Coal Field, Hancock County, Kentucky.

was to be installed within 400 ft of the Blan well to monitor groundwater quality in the lowermost underground source of drinking water. Oil and gas records were used to determine that the lowermost USDW was the undifferentiated Tar Springs Formation and Glen Dean Limestone. MW1 was drilled to a depth of 423 ft, approximately 40 ft below the defined USDW. No groundwater was encountered while drilling, and therefore the borehole was determined to be dry and was properly plugged according to Kentucky monitoring-well regulations (Kentucky Department of Environmental Protection, 1991). Accordingly, no groundwater-quality data were collected for the defined USDW. However, domestic water wells and springs located within a 2-mi radius of the Blan well—defined as the area of review—were identified and sampled to monitor any potential changes in groundwater quality associated with possible migration of CO₂ from deeper saline aquifers into shallow (less than 100 ft) freshwater aquifers.

Study Area Description

General Setting

The study area, as defined by the 2-mi radius around the Blan well, is located in east-central Hancock County and west-central Breckinridge County (Fig. 1). The Blan well is located approximately 1.5 mi northeast of Patesville and 4.5 mi southwest of Cloverport (Fig. 1). Geologically and physiographically, the study area is located along the eastern edge of the Western Kentucky Coal Field (Fig. 1).

Geology

The study area is located in the Cloverport 7.5-minute quadrangle (Bergendahl, 1965). Underlying bedrock deposits of interest as described by Bergendahl (1965) are, from youngest to oldest, the Caseyville Formation, Buffalo Wallow Formation, Tar Springs Formation, and Glen Dean Limestone. The Golconda Limestone, not described by Bergendahl (1965), underlies the Glen Dean Limestone. The lowermost USDW was determined to be associated with the undifferentiated Tar Springs Formation and Glen Dean Limestone.

The surficial bedrock unit beneath the Blan well and MW1 is the Caseyville Formation (Fig. 2), which ranges from a conglomeratic sandstone to a

massive, crossbedded sandstone interbedded with shale (Bergendahl, 1965; Greb and others, 1992). In the study area, perennial springs are associated with sandstones in the Caseyville Formation. Caseyville channel-fill sandstones cut through the underlying Buffalo Wallow Formation. The Buffalo Wallow consists of interbedded shale, sandstone, siltstone, and limestone, and ranges in thickness from 0 to 245 ft. The uppermost member of the Buffalo Wallow Formation is the Kinkaid Limestone, which ranges in thickness from 0 to 60 ft (Fig. 3). The Menard Limestone, a member of the Buffalo Wallow Formation, is approximately 50 ft thick in the study area (Fig. 3). The Vienna Limestone is the basal member of the Buffalo Wallow Formation and is 0 to 8 ft thick (Fig. 3).

Underlying the Buffalo Wallow Formation is the Tar Springs Formation, which is predominantly a massive crossbedded sandstone that forms cliffs in the study area, and ranges in thickness between 0 and 130 ft. The sandstone grades laterally into a shale within the study area and ranges in depth between 0 and 300 ft. The shale facies of the Tar Springs Formation was encountered beneath the Blan well and MW1 (Fig. 3). Perennial springs are associated with the sandstone facies of the Tar Springs. Below the Tar Springs Formation are the Glen Dean and Golconda Limestones, which are each 30 to 40 ft thick beneath the injection well site (Fig. 3).

Preliminary Water Well and Spring Search

A preliminary search of the Kentucky Groundwater Data Repository was conducted in November 2008 to locate potential shallow groundwater-monitoring sites. Five domestic water wells (DWW) and one domestic spring (DS) were located within the study area (Fig. 4). DWW3 is also listed in Faust and others (1980). The total depths of DWW1, DWW2, DWW3, and DWW4 indicate that all four wells were completed in the lower Caseyville and upper Buffalo Wallow Formations (Table 1). Well DWW5 has a reported total depth of 26 ft, and based on the mapped geology appears to be completed in alluvium deposits of Locust Creek (Bergendahl, 1965) (Table 1). Discharge data are not available for DS1. Available groundwater-quality data for the five wells and spring are listed in Table 2. Landowner contact information for

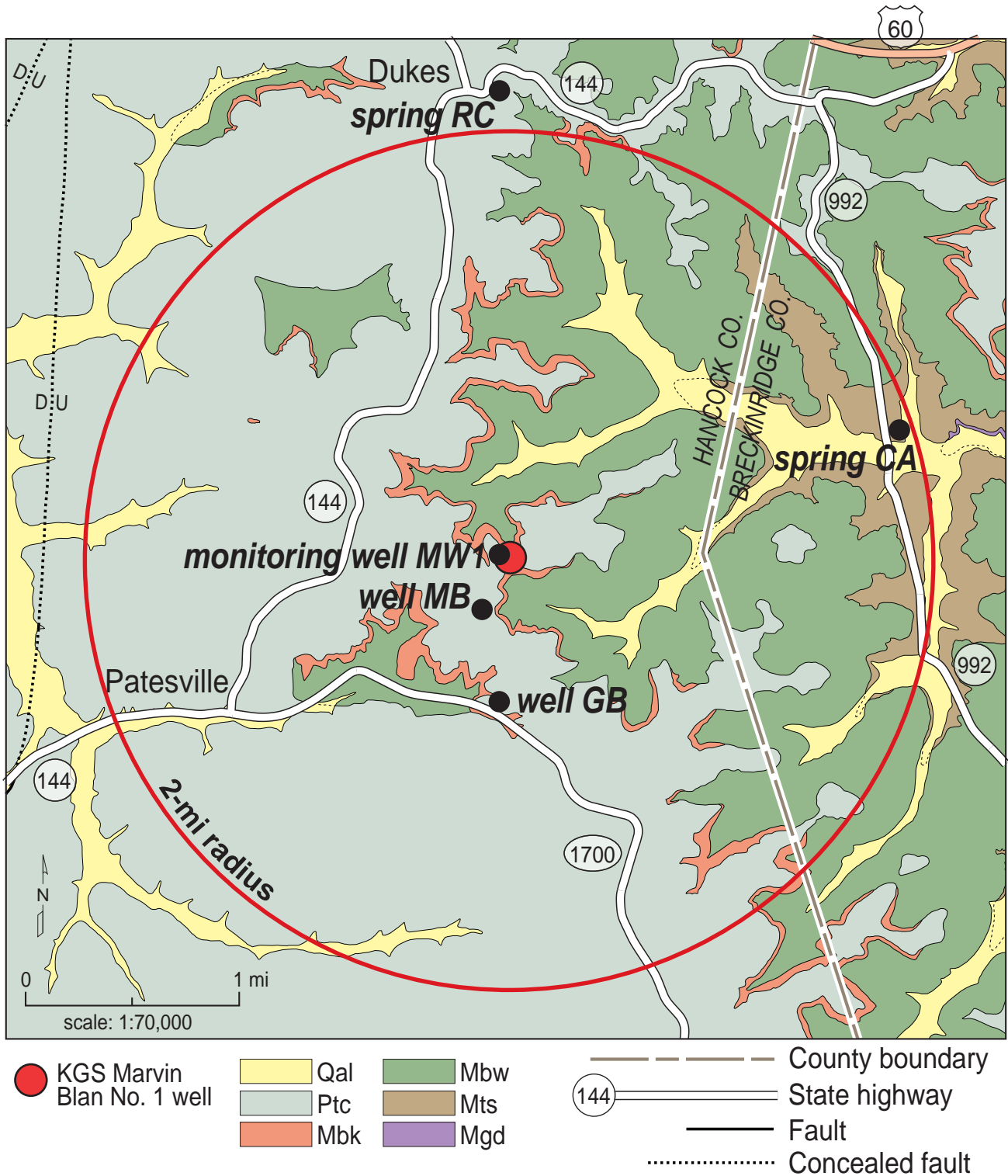


Figure 2. Location of KGS Marvin Blan No. 1, MW1, MB, and GB wells, springs CA and RC, and the 2-mi area of review (study area) in Hancock and Breckinridge Counties, Kentucky. Geologic units are the Quaternary alluvium (Qal), Tradewater and Caseyville Formations (Ptc), Kincaid Limestone Member of the Buffalo Wallow Formation (Mbk), Buffalo Wallow Formation (Mbw), Tar Springs Formation (Mts), and Glen Dean Limestone (Mgd). Geologic map modified from Bergendahl (1965).

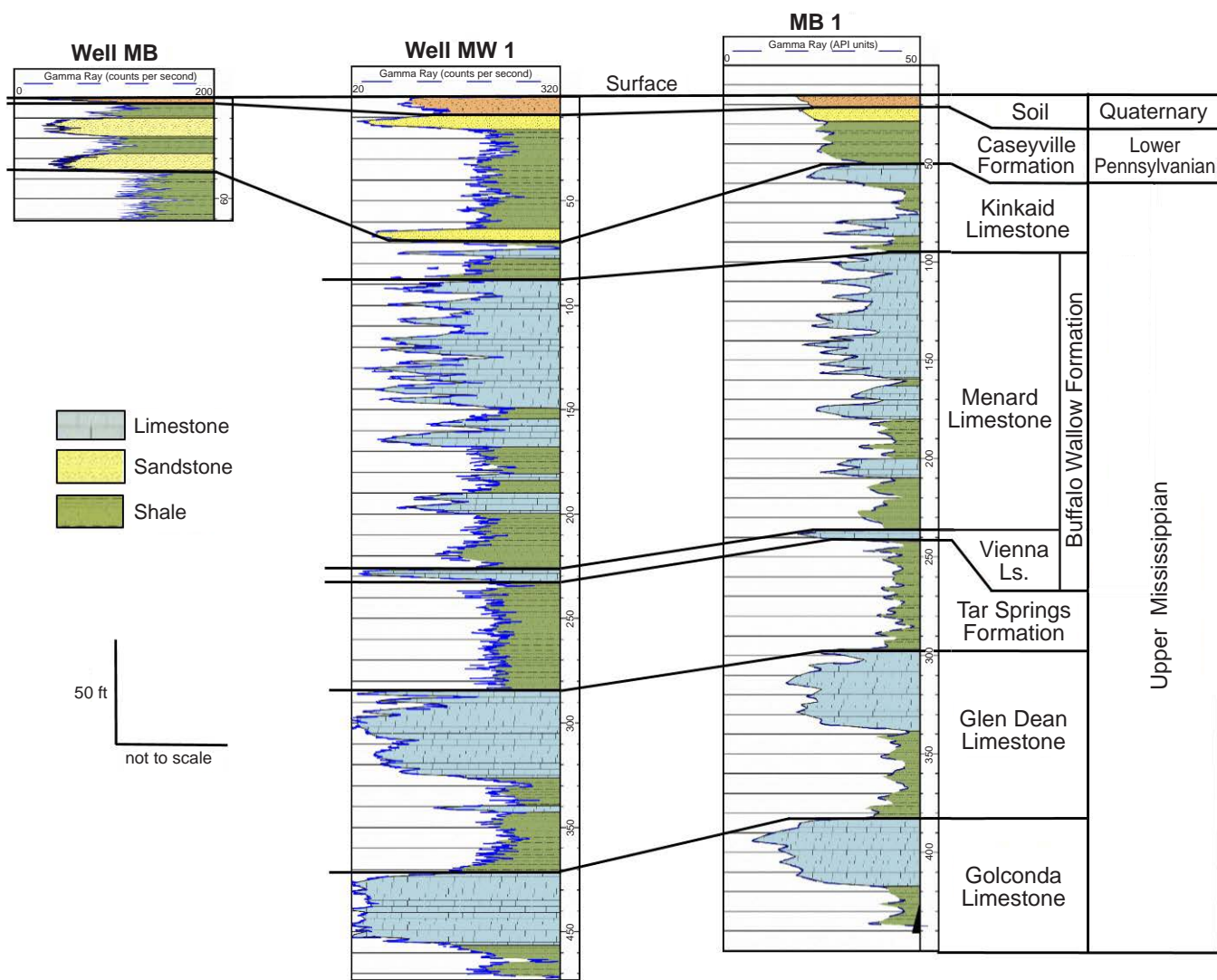


Figure 3. Correlation of shallow subsurface geology between Marvin Blan No. 1, MW1, and MB wells using gamma-ray logs. MW1 is located approximately 150 ft northwest of the Blan well (Fig. 2). Cross section modified from Bowersox and Williams (2009).

the five wells and one spring was not available. Therefore, these six sites were not used for shallow groundwater monitoring.

Discussions in November 2008 with the owner of the property on which the Blan well was located revealed that an abandoned domestic well (MB) is located approximately 1,500 ft southwest of the Blan well (Fig. 2). Well MB was drilled to a depth of 64 ft, and no historical groundwater-quality data were available for the well. Well MB was designated as a shallow groundwater-monitoring site for this project.

Sample Site Identification

Because only one suitable shallow groundwater monitoring site was identified during the preliminary search, additional efforts were needed to identify other monitoring sites. Hancock and Breckinridge Counties land assessor records were used to identify landowners in the study area. Two hundred twenty-four different land parcels were identified within the study area, and in January 2009, letters were mailed to the owners of 184 parcels asking them to participate in a survey about wells and springs. Addresses for 40 of the landown-

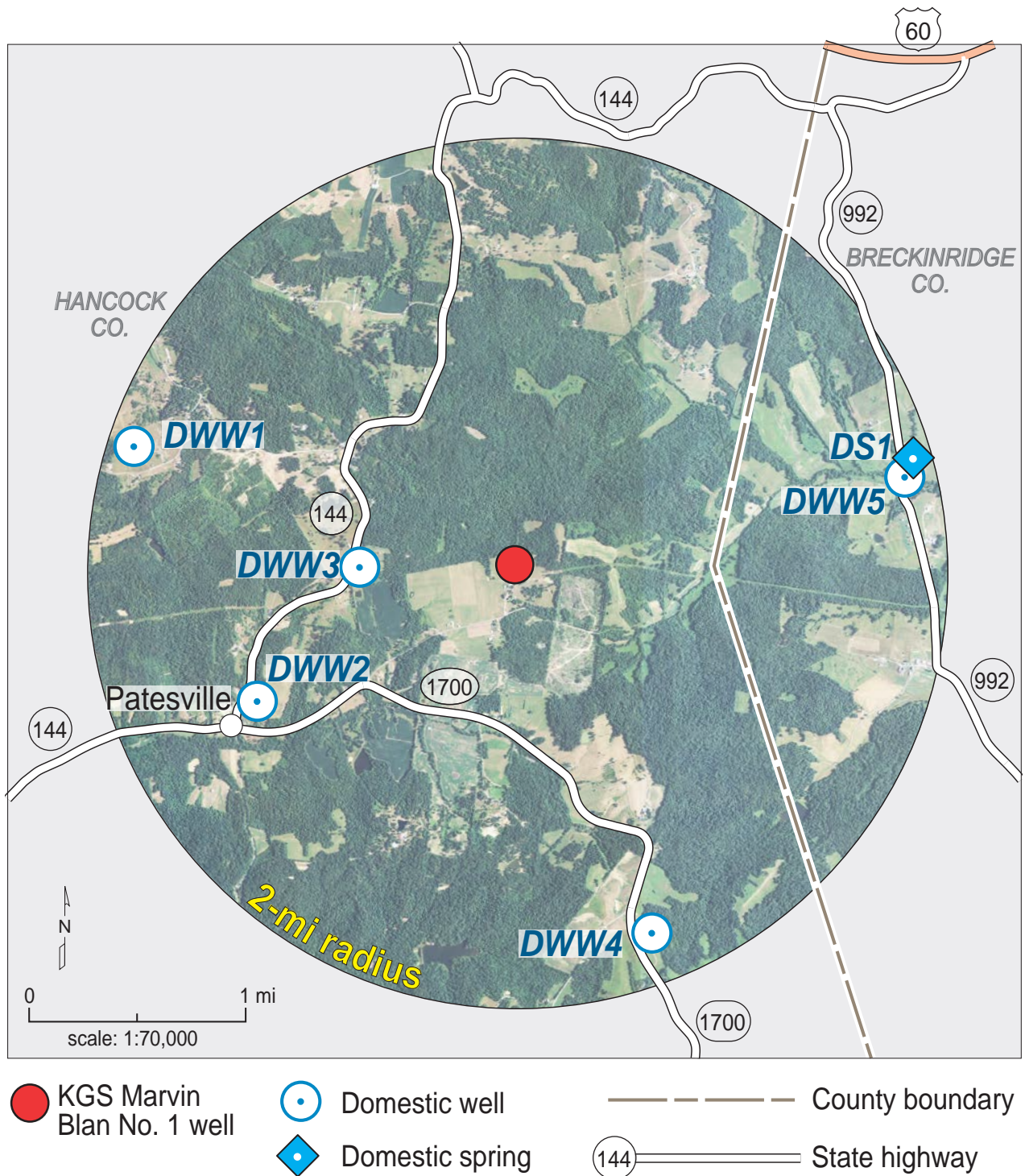


Figure 4. Locations of domestic water wells (DWW1 through DWW5) and domestic spring (DS1) identified during the preliminary water well and spring search.

ers were unknown. A total of 69 surveys were returned with well and spring information, but only one domestic well and two domestic springs were

identified as potential monitoring sites. In May 2009, each site was inspected and access was confirmed with each landowner. Well GB and springs

Table 3. Identification, location, and discharge data for the shallow groundwater monitoring sites and monitoring well MW1. NA=not applicable. r=Data reported by property owner.

AKGWA Number	Site Name	Total Depth (ft)	Latitude (NAD 83)	Longitude (NAD 83)	Yield or Discharge (gal/min)
00065947	well MB	64	37.788735	-86.696813	1
00065945	well GB	35 ^r	37.782470	-86.695500	10 ^r
90003300	spring CA	NA	37.801204	-86.660571	0.5–6.0
90003301	spring RC	NA	37.824580	-86.696230	0.5–1.3
NA	monitoring well MW1	423	37.792594	-86.694720	0

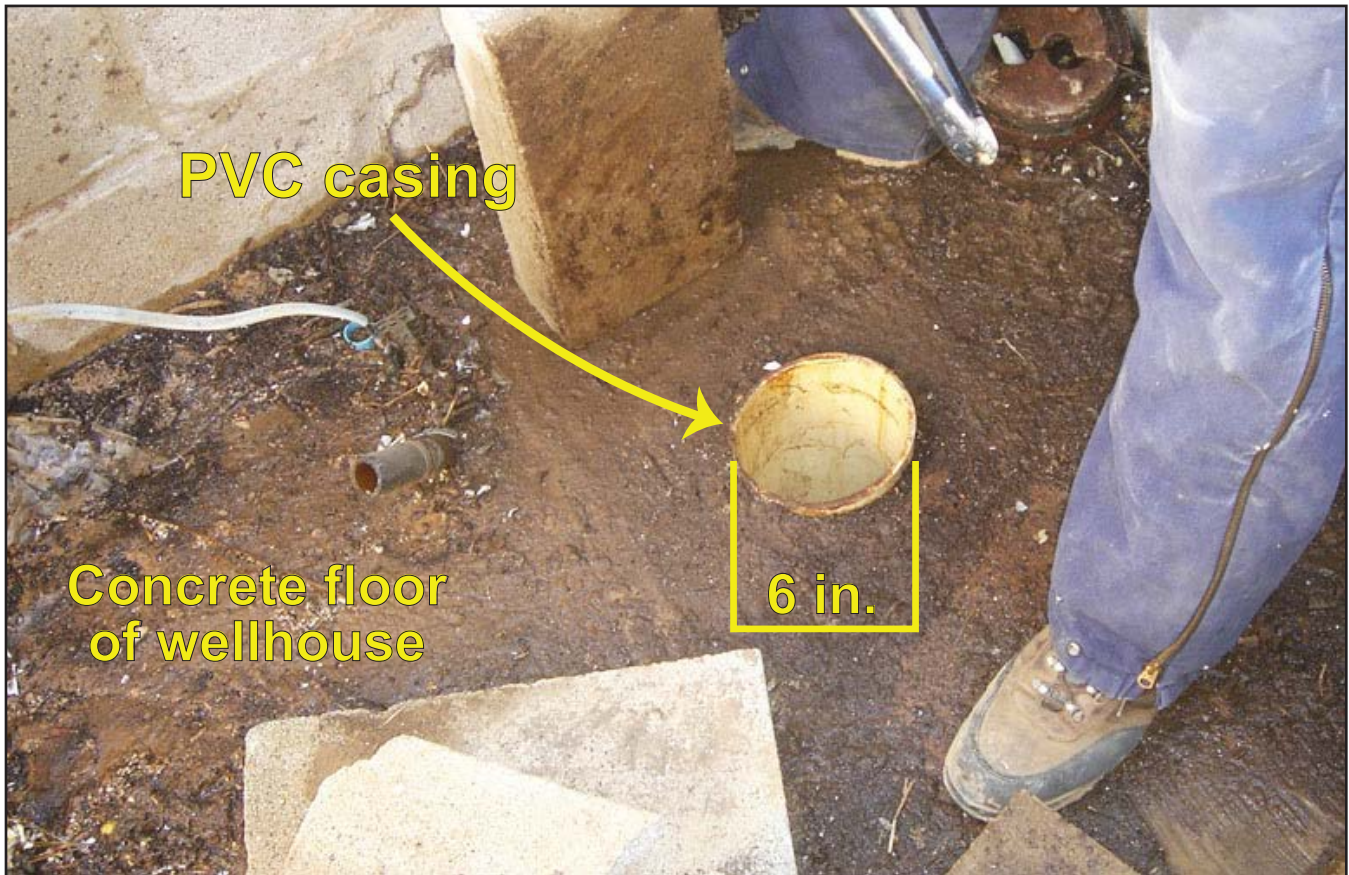


Figure 5. PVC casing in well MB. The casing is flush with the concrete floor of the wellhouse.

mately 150 ft northwest of the Blan well (Fig. 2) in April 2009 to a depth of 423 ft (Table 4), approximately 40 ft below the lowermost USDW (undifferentiated Tar Springs Formation and Glen Dean Limestone) (Fig. 3). Because the shale facies of the Tar Springs Formation was present beneath the injection site, no groundwater-quality data were collected for the USDW. The borehole was properly plugged according to Kentucky monitoring-well regulations (Kentucky Department of Environ-

mental Protection, 1991). As instructed by the EPA, we did not install additional monitoring wells.

Methodology

As stipulated by the EPA underground injection control permit, the four monitoring sites were sampled prior to CO₂ injection to determine baseline conditions and sampled quarterly after the injection. Prior to CO₂ injection, well MB was sampled seven times, and well GB, spring CA, and spring RC were sampled five times (Table 4). All

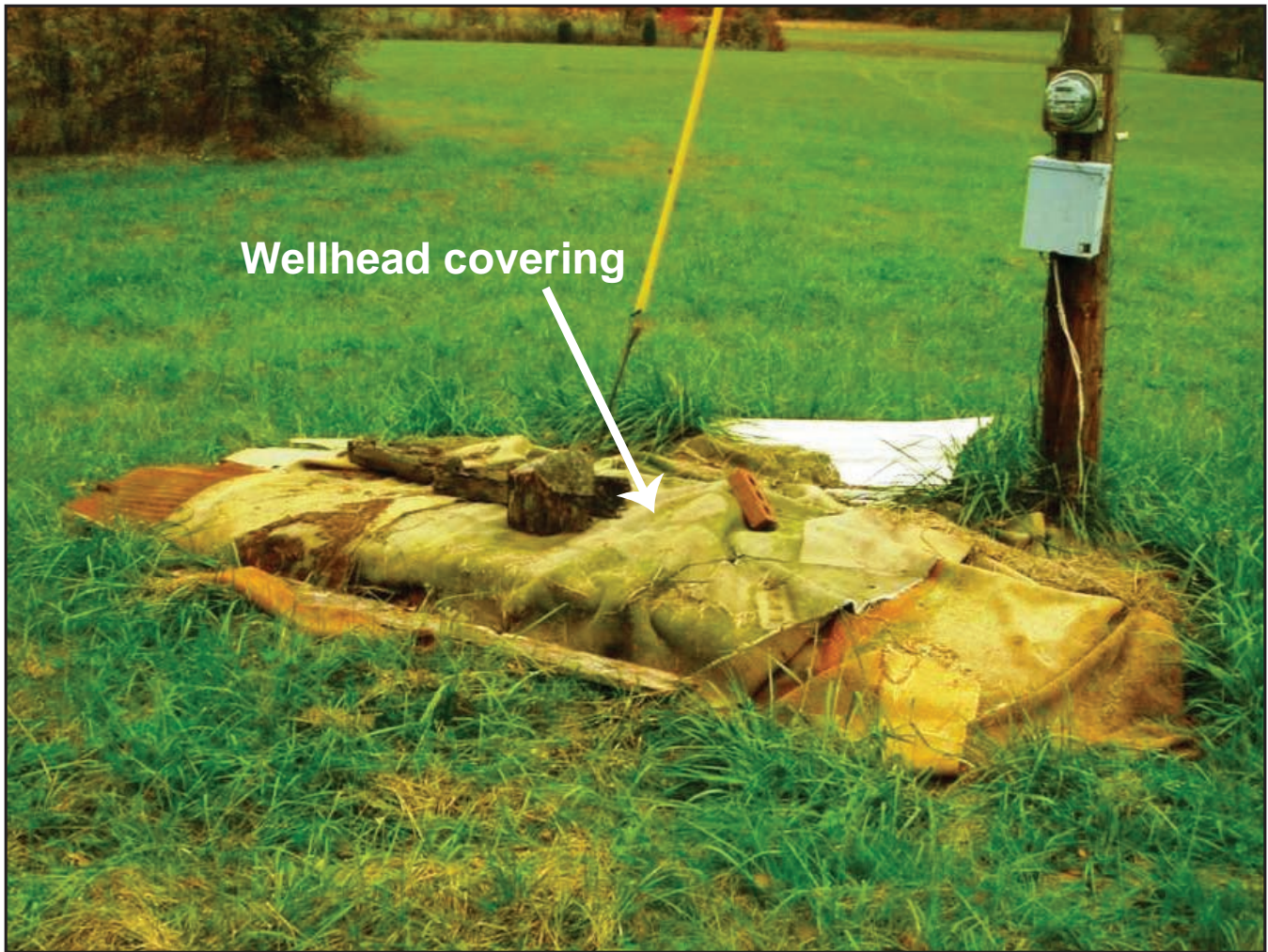


Figure 6. Frost-proof covering over well GB. The brick on the wellhead covering is approximately 8 in. long.

sites were sampled four times after the phase I injection and seven times after the phase II injection (Table 5). Spring RC was sampled one additional time on August 16, 2012. Sampling was attempted at well MB on August 16, 2012, but the well pumped dry during sampling and did not recharge within the next hour. Therefore, field measurements were not recorded and samples were not collected for well MB.

Groundwater sampling, as prescribed by the phase I underground injection control permit, was to be discontinued in April 2012. However, because of phase II CO₂ injection, the permit was modified by the EPA to extend quarterly sampling for 2 yr after plugging and abandonment of the Blan well. This would have extended sampling through October 2013. After informing well and spring own-

ers of this extension, however, all requested that sampling be discontinued. Consequently, the last time well GB and spring CA were sampled was on May 9, 2012, and the last time well MB and spring RC were sampled was on August 16, 2012 (Table 4).

The underground injection control permit also required that each site be sampled for pH, bicarbonate, total dissolved solids, and turbidity. In addition to the four mandated chemical parameters, each site was sampled periodically for a full suite of chemical constituents, total CO₂, dissolved inorganic carbon, and delta carbon-13 of the dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) (Table 4). All groundwater-quality data collected during this project were entered into the Kentucky Groundwater Data Repository and made available online at kgs.uky.edu/kgsweb/DataSearching/watersearch.asp.

Table 4. Chemical constituents sampled at wells MB and GB and springs CA and RC. Blank cells indicate that the chemical constituents were not sampled for that date. "All" indicates that the respective chemical constituents were measured at all four monitoring sites. For some sampling dates, some chemical constituents were measured only at well MB and spring RC. On April 15, 2009, $\delta^{13}\text{C}_{\text{DIC}}$ samples were collected at all four sites, but the glass sample bottle used at spring RC broke during shipping and its sample was not analyzed.

<i>CO₂ Injection Phase</i>	<i>Sampling Date</i>	<i>Sampling Event</i>	<i>pH, HCO₃⁻, Total CO₂</i>	<i>pH, HCO₃⁻, Total CO₂, TDS, Turbidity</i>	<i>Dissolved Inorganic Carbon</i>	<i>Chloride and Sulfate</i>	<i>Total Dissolved Solids</i>	<i>$\delta^{13}\text{C}_{\text{DIC}}$</i>
Preinjection (Baseline)	12/3/2008	1	MB		MB	MB	MB	
	1/12/2009	2	MB		MB	MB	MB	MB
	4/15/2009	3		all	all	all	all	all
	5/5/2009	4		all	all	all	all	
	5/19/2009	5		all	all	all	all	all
	5/28/2009	6		all				
	7/20/2009	7		all	all	all	all	
Post-Phase I Injection (1st–4th Quarter)	11/16/2009	8		all				
	2/23/2009	9		all				
	5/25/2010	10		all				
	8/16/2010	11		all	all	all	all	all
Post-Phase II Injection (5th–12th Quarter)	11/15/2010	12		all				
	2/22/2011	13		all				
	5/17/2011	14		all				
	8/30/2011	15		all	all	all	all	all
	11/14/2011	16		all				
	2/20/2012	17		all				
	5/9/2012	18		all				
	8/16/2012	19		RC	RC	RC	RC	

Water Well Sampling

Groundwater data were collected from wells MB and GB from December 2008 through May 2012 (Table 4). Field measurements and groundwater samples were collected in accordance with U.S. Geological Survey guidelines (U.S. Geological Survey, 1980). Well MB was purged and sampled using a 2-in.-diameter submersible Fultz¹ pump at a rate of 1 gal/min. Prior to sampling well MB, the pump was decontaminated on site by purging with 10 gal of deionized water. Well GB was purged and sampled using the existing submersible pump. Well GB samples were collected from

a frostless hydrant. The existing plumbing system was purged for 10 min prior to recording any field measurements.

Field measurements (specific conductance, pH, temperature, dissolved oxygen, and oxidation-reduction potential) were recorded using a Horiba U-22 water-quality monitoring system with a flow-through chamber. Wells MB and GB were pumped until field measurements stabilized and then samples were collected. The monitoring system was calibrated daily during sampling using procedures prescribed by the manufacturer.

¹The use of trade or product names is for descriptive purposes only and does not imply endorsement by the Kentucky Geological Survey.

Table 5. Summary of analyses and methods for water chemistry and properties.

<i>Analyte</i>	<i>Method</i>	<i>Preservative</i>	<i>Laboratory</i>
Total dissolved metals: aluminum barium beryllium calcium iron magnesium manganese potassium silicon sodium strontium	EPA 200.7 and SW846– 6010A, B inductively coupled plasma	filter, nitric acid, 4°C	KGS
chloride and sulfate	EPA 300.0 ion chromatography	filter, 4°C	KGS
alkalinity	EPA 310.1	4°C	KGS
bicarbonate	calculated from alkalinity	4°C	KGS
total dissolved CO ₂	ASTM D513A gas-sensing electrode	4°C	KGS
dissolved inorganic carbon	ASTM D513B CO ₂ coulometer	filter, 4°C	KGS
total dissolved solids	EPA 160.1 gravimetric	filter, 4°C	KGS
turbidity	EPA 180.1	4°C	KGS
δ ¹³ C _{DIC}	Spötl (2005)	4°C	ISOTECH

Spring Sampling

Groundwater data were collected from springs RC and CA from April 2009 through August 2012 (Table 4). Field measurements and groundwater samples were collected in accordance with U.S. Geological Survey guidelines (U.S. Geological Survey, 1980). As with the well measurements, a Horiba U-22 water-quality monitoring system was used to measure water properties (specific conductance, pH, temperature, dissolved oxygen, and oxidation-reduction potential) in the field.

Because each spring was used as a domestic water supply, spring water was piped from the discharge point to a reservoir. Field measurements and samples were taken from groundwater discharging from these plumbed systems (Fig. 7). At spring RC, the monitoring system was placed in a 2.5-gal bucket that was placed beneath the discharge pipe and acted as a flow-through chamber. Field measurements were recorded until they stabilized and then samples were collected. At spring CA, a 2.5-gal bucket was filled with discharge water, and field measurements were recorded three to four times using the monitoring system.

Analytical Methods

All laboratory analyses were in accordance with either EPA methods or methods widely accepted in the literature, such as ASTM methods. Sample splits were prepared in the field and transported to the appropriate laboratory in bottles certified pre-cleaned by the manufacturer. For dissolved-constituent analysis, filtration was performed in the field using high-capacity inline filters (0.45-µm pore size). If sample preservation was required by analysis protocol, the samples were preserved at the time of collection and kept at a temperature of 4°C until delivered to the appropriate laboratory.

Bulk chemistry and water properties were measured at the KGS laboratory and δ¹³C_{DIC} was measured at ISOTECH Laboratories Inc. (Table 5).

Quality Control

Equipment blanks, field blanks, and charge-balance analysis were used to determine potential sampling or analytical errors. Prior to deploying the Fultz pump into well MB, equipment blanks were collected by sampling deionized water

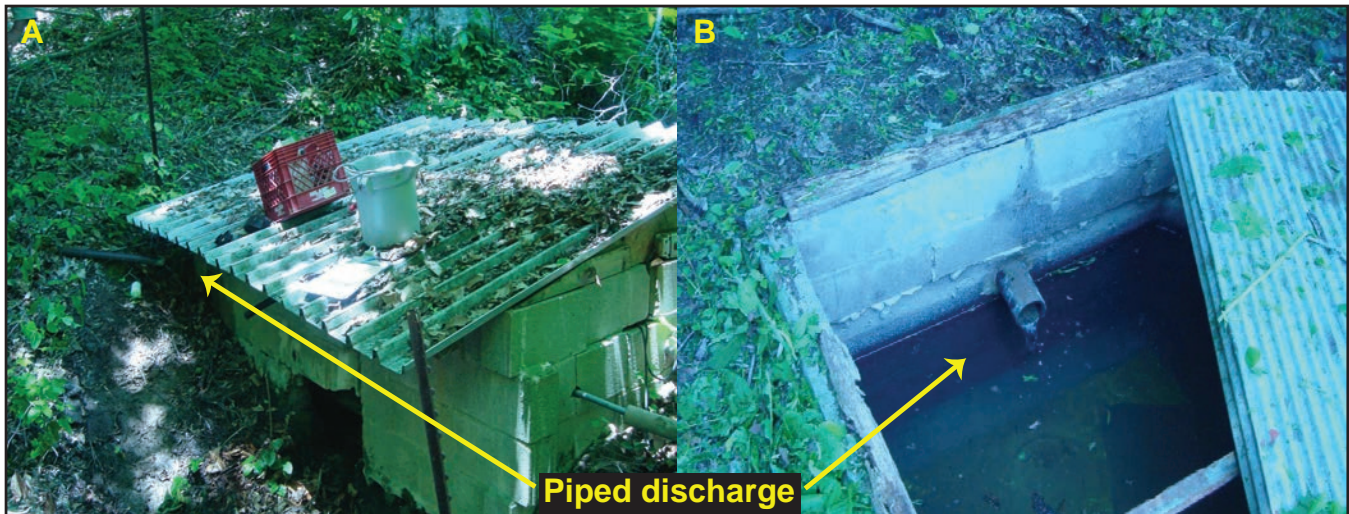


Figure 7. Sample points for spring RC (A) and spring CA (B).

pumped through the decontaminated pump. One equipment blank was collected during six of the 19 sampling events. If required, equipment blank samples were preserved in the field as described in Table 5. Analytical results for all equipment blank samples indicate that analyte concentrations are

either below or just slightly greater than method detection limits (Table 6).

Field blanks were collected by filling sample bottles with deionized water at one of the sampling sites. If required, field blank samples were preserved in the field as described in Table 5. One field blank was collected during 14 of the 19 sam-

Table 6. Summary of analytical results for equipment blank samples at well MB. The “<” sign indicates that the analyte concentration was below the method detection limit.

Analyte	Number of Samples	Minimum	Maximum	Method Detection Limit	Unit
aluminum	4		<	0.061	mg/L
barium	4		<	0.003	mg/L
beryllium	4		<	0.001	mg/L
bicarbonate	6		<	4	mg/L CaCO ₃
calcium	4	0.070	0.190	0.002	mg/L
chloride	4		<	1	mg/L
dissolved inorganic carbon	2		<	3.8	mg/L
iron	4	0.005	0.080	0.002	mg/L
magnesium	4	0.005	0.050	0.001	mg/L
manganese	4	<	0.030	0.001	mg/L
potassium	4		<	0.191	mg/L
silicon	4	<	0.050	0.009	mg/L
sodium	4	<	0.340	0.009	mg/L
strontium	4		<	0.01	mg/L
sulfate	4		<	5	mg/L
total dissolved solids	4		<	10	mg/L
total CO ₂	6		<	13.8	mg/L
turbidity	4	0.2	0.4	0.1	NTU

Table 7. Summary of analytical results for field blank samples. The “<” sign indicates that the analyte concentration was below the method detection limit.

Analyte	Number of Samples	Minimum	Maximum	Method Detection Limit	Unit
aluminum	5		<	0.061	mg/L
barium	5		<	0.003	mg/L
beryllium	5		<	0.001	mg/L
bicarbonate	13	<	5	4	mg/L CaCO ₃
calcium	5	<	0.060	0.002	mg/L
chloride	5		<	1	mg/L
dissolved inorganic carbon	3		<	3.8	mg/L
iron	5	<	0.009	0.002	mg/L
magnesium	5	<	0.017	0.001	mg/L
manganese	5		<	0.001	mg/L
potassium	5	<	0.330	0.191	mg/L
silicon	5		<	0.009	mg/L
sodium	5	<	0.390	0.058	mg/L
strontium	5		<	0.01	mg/L
sulfate	5		<	5	mg/L
total dissolved solids	5		<	10	mg/L
total CO ₂	12		<	13.8	mg/L
turbidity	12	0.2	0.7	0.1	NTU

pling events. Analytical results for all of the field blank samples indicate that analyte concentrations are either below or just slightly greater than MDL's (Table 7).

Analytical accuracy of the major anions and cations was addressed by charge-balance analysis. Charge balance among measured cation and anion concentrations provides an important criterion for determining the quality of water-chemistry measurements (Freeze and Cherry, 1979). Assuming that the analyzed waters are electrically neutral overall, the electrical charges contributed by cations and anions (reported as milliequivalents per liter) should be close to zero. Large departures indicate that a major anion or cation was not includ-

ed in the analysis or that there were problems with sampling, sample preservation, and handling, or laboratory errors. Charge balance was determined using the following equation:

$$\% \text{ Imbalance} = 100 \times (\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions}). \quad (1)$$

Charge balances of 27 samples from the four sites show that charge-imbalance errors were small, with 89 percent and 74 percent of the samples less than or equal to a 10 percent or 5 percent imbalance error, respectively (Table 8). The dilute character of the well and spring water makes any analytical error more pronounced, which could be the reason for the greater imbalance seen in three of the 27 samples. One sample from well MB had

Table 8. Summary of charge imbalances for samples collected at the four monitoring sites. The last two columns represent the percentage of samples having charge imbalances equal to or less than 10 and 5 percent, respectively.

Sites	Number of Samples	≤ 10 Percent	≤ 5 Percent
wells	14	93	71
springs	13	85	77
all	27	89	74

an imbalance of 21.6 percent and two samples from spring RC had imbalances greater than 10 percent (14.4 and 12.0 percent).

Results

Measurements at the four monitoring sites provided the opportunity to document the variation in shallow groundwater bulk and isotopic chemistry before, during, and after CO₂ injection. The preinjection measurements provide the opportunity to document departures from baseline values that are attributed to either natural variation or influence from CO₂ that migrated upward.

Groundwater Type

Major anion and cation concentrations were plotted on tertiary diagrams to determine the dominant groundwater type at each site (Piper, 1944). Groundwater sampled at well MB varied considerably in composition, ranging from a calcium-bicarbonate type to a sodium-mixed anion type (Fig. 8). Overall, the changes in groundwater type are not systematic over time, nor do they correlate with CO₂ injection events. The variation in groundwater type at well MB is most likely associated with the well construction, in which the casing is screened the entire length of the wellbore, which allows commingling of groundwater from different aquifers. In addition, the property owner reported that the well water had a history of becoming turbid after large precipitation events. This suggests that well MB is leaking, thereby allowing surface water to enter the wellbore during and after precipitation events.

Groundwater from well GB and spring CA was consistently a calcium-bicarbonate type (Fig. 9). No geochemical changes were observed among samples collected before or after CO₂ injection; therefore, there is no evidence for CO₂ migrating upward into the shallow groundwater system.

The dominant type of groundwater seen at spring RC is sodium-bicarbonate (Fig. 9). With the exception of the sample collected on 8/30/2011 (sampling event 15), all sulfate concentrations were below the MDL. The sulfate concentration for 8/30/2011 was 10.6 mg/L, which explains the outlier in the anion field of the Piper diagram (Fig. 9). Minor variations in calculated bicarbonate concentrations (6 to 15 mg/L) are not systematic over

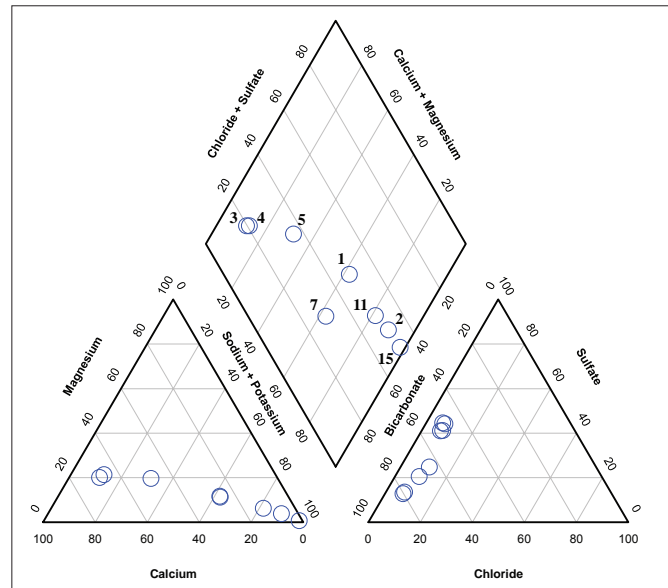


Figure 8. Piper diagram showing groundwater composition for well MB. The number next to the open circles in the diamond-shaped field indicates the sampling event listed in Table 5. Sampling events 1 through 7 occurred before CO₂ injection and events 11 and 15 after CO₂ injection.

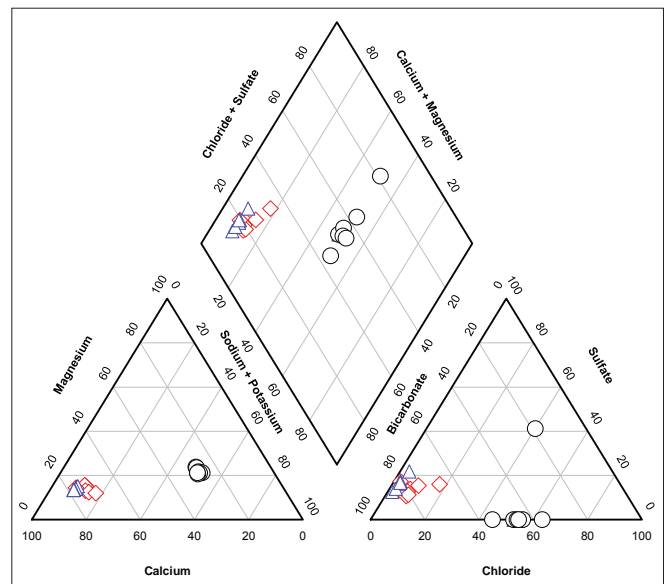


Figure 9. Piper diagram showing groundwater composition for well GB (blue triangles), spring CA (red diamonds), and spring RC (black circles).

time and could be attributed to alkalinity being determined in the laboratory rather than in the field. Therefore, geochemical changes seen at spring RC do not appear to be associated with injected CO₂ migrating upward into the shallow groundwater system.

pH

Groundwater in the United States generally has a pH value ranging between 6.0 and 8.5 (Hem, 1992). Field pH measurements at the four monitoring sites ranged between 4.58 and 7.82 (Table 9). The lowest pH values (4.58–5.52) were recorded at spring RC, and suggest there is little buffering from carbonate minerals in the Caseyville Formation sandstone aquifer.

Laboratory and field tests show that when CO₂ is introduced into either a fresh or saline aquifer, the dissolution of CO₂ and attendant dissociation reactions occur rapidly (days to weeks) and, in turn, lower the pH (1–3 pH units) (Smyth and others, 2009; Frailey and others, 2012). Comparison of pre-CO₂ injection to post-CO₂ injection pH values shows no overall change (decrease) at any of the monitoring sites (Fig. 10). The slight changes in pH values at the four sites appear to be related to seasonal variations. Typically, the highest pH values occur during winter, and the lowest values generally occur during late spring or summer (Fig. 10). The lack of change in pH from preinjection values indicates that CO₂ injectate did not migrate upward into the shallow groundwater aquifer at the four monitored sites.

Bicarbonate, Total CO₂, Dissolved Inorganic Carbon, and δ¹³C_{DIC}

Alkalinity is the ability of water to react with hydrogen ions and neutralize acidity. This capacity is controlled in many environments by the presence of carbonate and bicarbonate ions, and can be described in terms of bicarbonate concentration. Bicarbonate concentrations in groundwater vary greatly and are controlled mostly by the dissolution of carbonate rock-forming minerals such as calcite. Research by Frailey and others (2012) and Kharaka and others (2006) has shown that with an influx of CO₂ into a brine aquifer, bicarbonate concentration can increase dramatically (a range of 1,500 to

3,000 mg/L) over a short period (days). Based on these field studies and research by Smyth and others (2009), we can assume that if injectate CO₂ was introduced into a freshwater aquifer, bicarbonate concentration would increase significantly.

Bicarbonate concentrations for the four monitoring sites ranged from 6 to 529 mg/L (Table 10). The lowest bicarbonate concentrations (6–16 mg/L) were associated with groundwater at spring RC and the highest concentrations (257–529 mg/L) were in groundwater at well MB (Table 10). Well MB showed the most variability in bicarbonate concentration over time. Post-injection bicarbonate concentrations increased more than 200 mg/L from preinjection concentrations (Fig. 11). Bicarbonate concentration rose prior to each injection event, spiked to just over 500 mg/L, and then dropped back to preinjection concentrations (Fig. 11). Total CO₂ concentration followed a trend similar to that of bicarbonate (Fig. 12). Dissolved inorganic carbon concentrations increased after injection (Fig. 13).

Because pH values remained at or above 7 at well MB (Fig. 10), the trends in bicarbonate, total CO₂, and dissolved inorganic carbon are most likely related to seasonal changes and not the presence of injectate CO₂. In 2009 and 2010, bicarbonate and total CO₂ concentrations at well MB increased between July and February (wet season) and then decreased in May (Figs. 11 and 12, respectively). Both analytes increased again between May 2010 and November 2011. Bicarbonate concentrations plateaued in 2011, which was a near-record year for precipitation in western Kentucky. Elevated bicarbonate, total CO₂, and dissolved inorganic carbon at well MB all correlate with wet-season events. In contrast, bicarbonate, total CO₂, and dissolved inorganic carbon concentrations were consistent throughout the monitoring period at the other three sites (Figs. 11–13). The contrast in geochemical behavior is likely attributable to leakage in well MB, which allowed meteoric water to infiltrate the borehole.

The δ¹³C_{DIC} values for groundwater at the four monitoring sites were generally consistent over time (Fig. 14). The δ¹³C_{DIC} values from wells MB and GB and spring CA ranged

Site	Number of Measurements	Minimum	Mean	Maximum	Standard Deviation
GB	16	6.37	6.94	7.38	0.27
MB	18	6.32	7.24	7.82	0.43
CA	16	6.27	6.97	7.53	0.32
RC	17	4.58	5.10	5.52	0.30

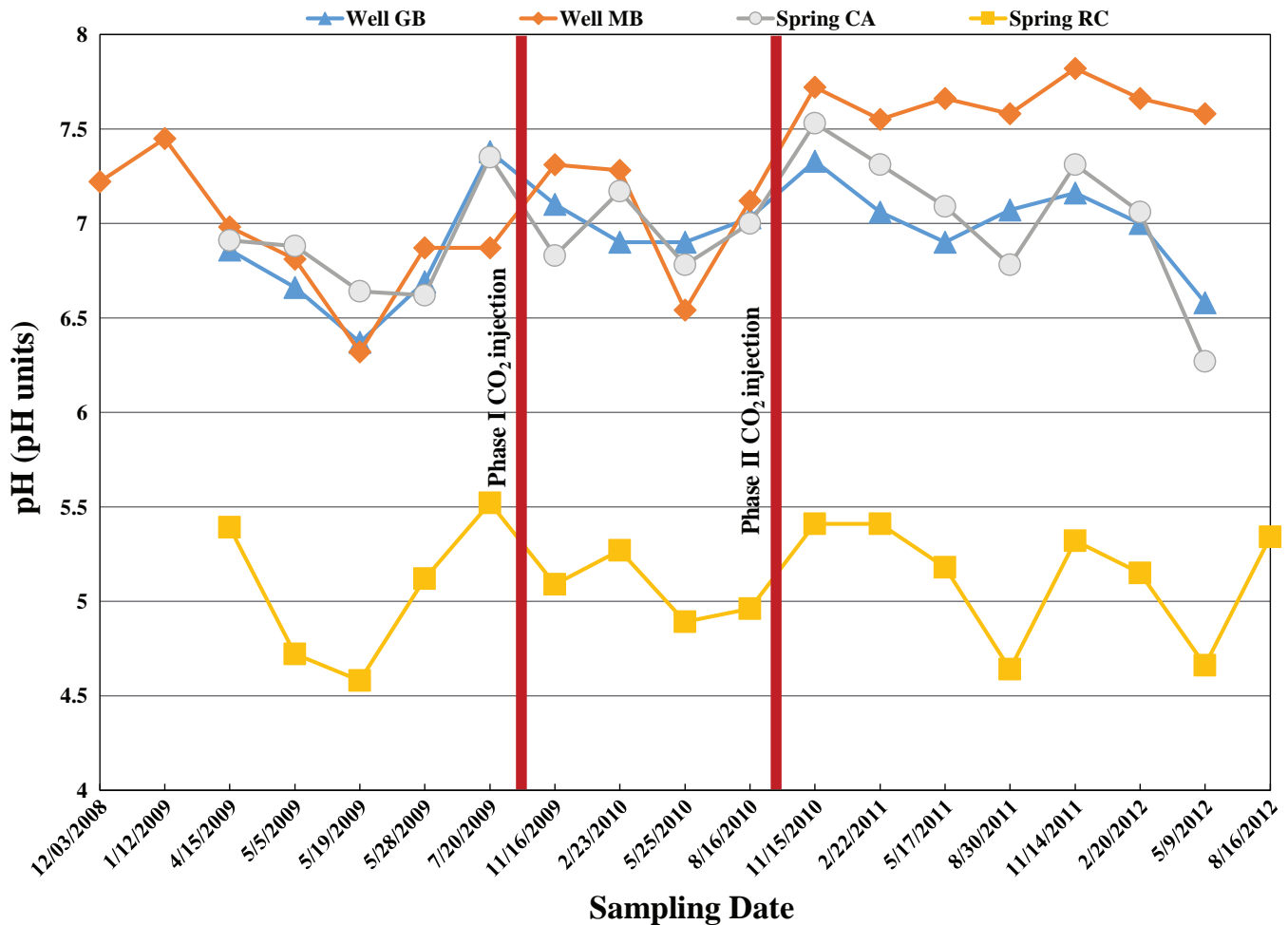


Figure 10. pH values over time for wells GB and MB and springs CA and RC. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

from -11.20 to -15.34 per mil (relative to Vienna Pee Dee Belemnite) and fall in the range of most natural groundwater (Sack and Sharma, 2013). The $\delta^{13}\text{C}_{\text{DIC}}$ value for groundwater at spring RC ranged from -22.30 to -22.73 per mil, which is less enriched than samples from the other three sites and most natural groundwater (Sack and Sharma, 2013). Relatively depleted $\delta^{13}\text{C}_{\text{DIC}}$ values at spring RC suggest the absence of carbonate minerals in sandstones of the Caseyville Formation. The possible lack of carbonate minerals might also account for the low pH values (Fig. 10), and low bicarbonate (Fig. 11), total CO₂ (Fig. 12), and dissolved inorganic carbon (Fig. 13) concentrations at spring RC relative to the other sites. Dissolved organic carbon was not analyzed, but might have been useful in

determining the relative contribution of an organic carbon source.

Even though isotopic values at wells MB and GB and spring CA are more enriched than at spring RC, they are still approximately 10 per mil lighter than the injectate CO₂, which has a $\delta^{13}\text{C}_{\text{CO}_2}$ value of -4.1 per mil (Marty Parris, Kentucky Geological Survey, unpublished data, 2008) (Fig. 14). For wells MB and GB and spring CA, $\delta^{13}\text{C}_{\text{DIC}}$ values are similar to local atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ and local soil gas $\delta^{13}\text{C}_{\text{CO}_2}$ values of -13 to -21 per mil measured in October 2008 (Marty Parris, Kentucky Geological Survey, unpublished data) (Fig. 14). The similarity reflects the collective zone of influence of soil microbe respiration, dissolution of carbonate minerals, and atmospheric CO₂ on the $\delta^{13}\text{C}$ composition

Table 10. Statistical summary for bicarbonate, dissolved inorganic carbon, and total CO₂ concentrations at the four monitoring sites. The “<” sign indicates that the analyte concentration was below the stated method detection limit.

Analyte	Site	Number of Measurements	Minimum	Mean	Maximum	Standard Deviation
bicarbonate	MB	16	247	390	529	115
	GB	16	123	177	213	23
	CA	16	149	177	205	20
	RC	17	6	9	16	3
dissolved inorganic carbon	MB	8	48	69	105	19
	GB	6	33	36	38	2
	CA	6	31	35	43	4
	RC	7	< 4	9	17	5
total CO ₂	MB	18	168	288	452	90
	GB	16	121	145	178	17
	CA	16	97	141	178	21
	RC	17	26	50	67	12

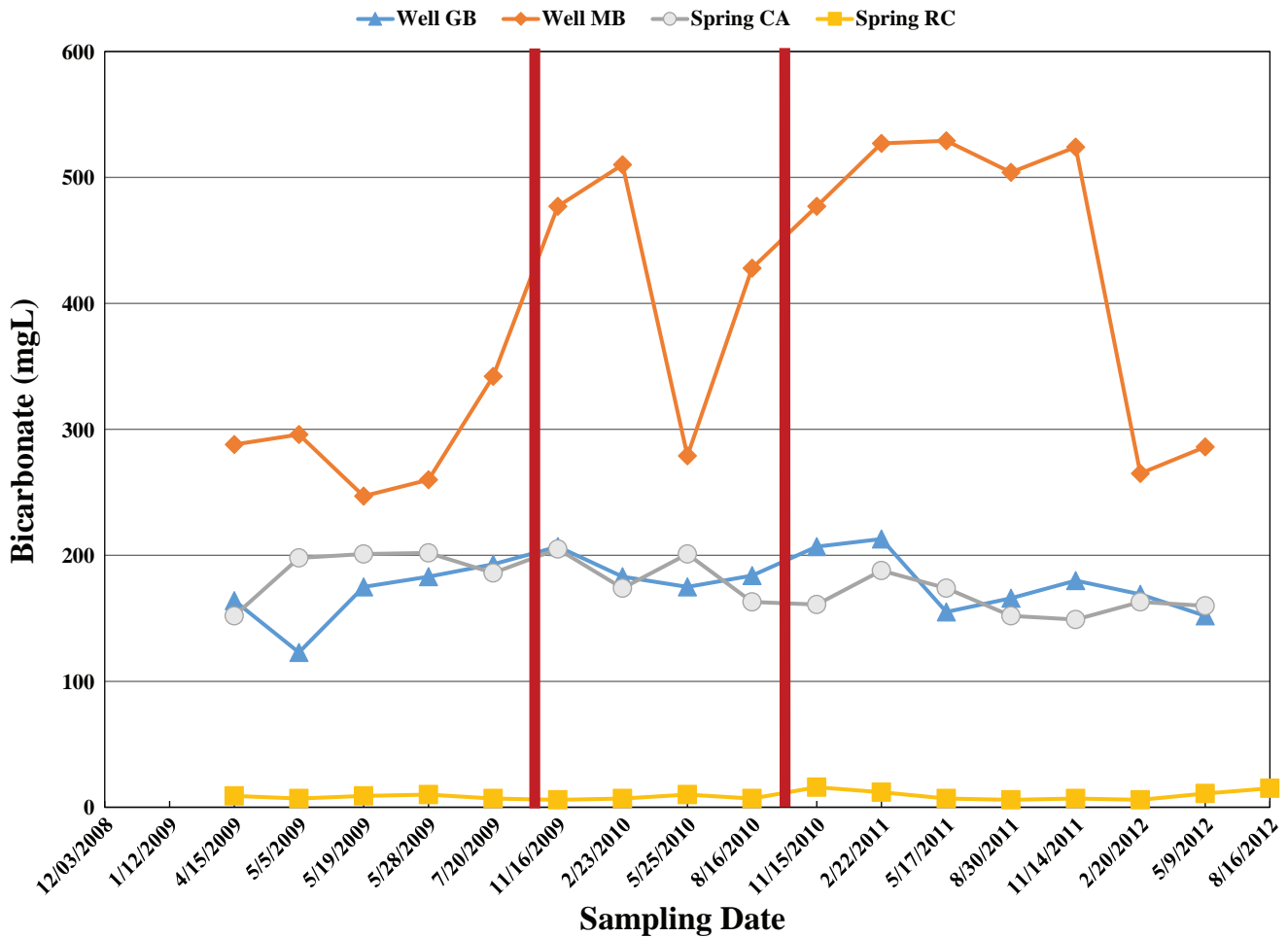


Figure 11. Bicarbonate concentrations over time for wells GB and MB and springs CA and RC. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

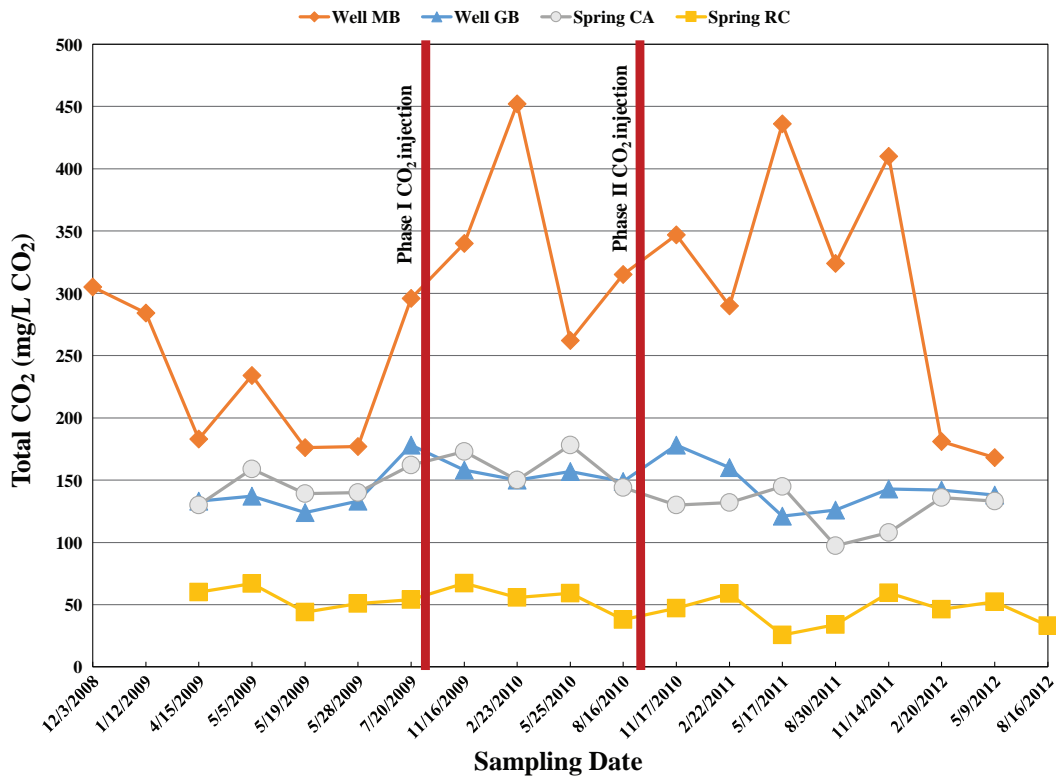


Figure 12. Total CO₂ concentrations over time for wells GB and MB and springs CA and RC. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

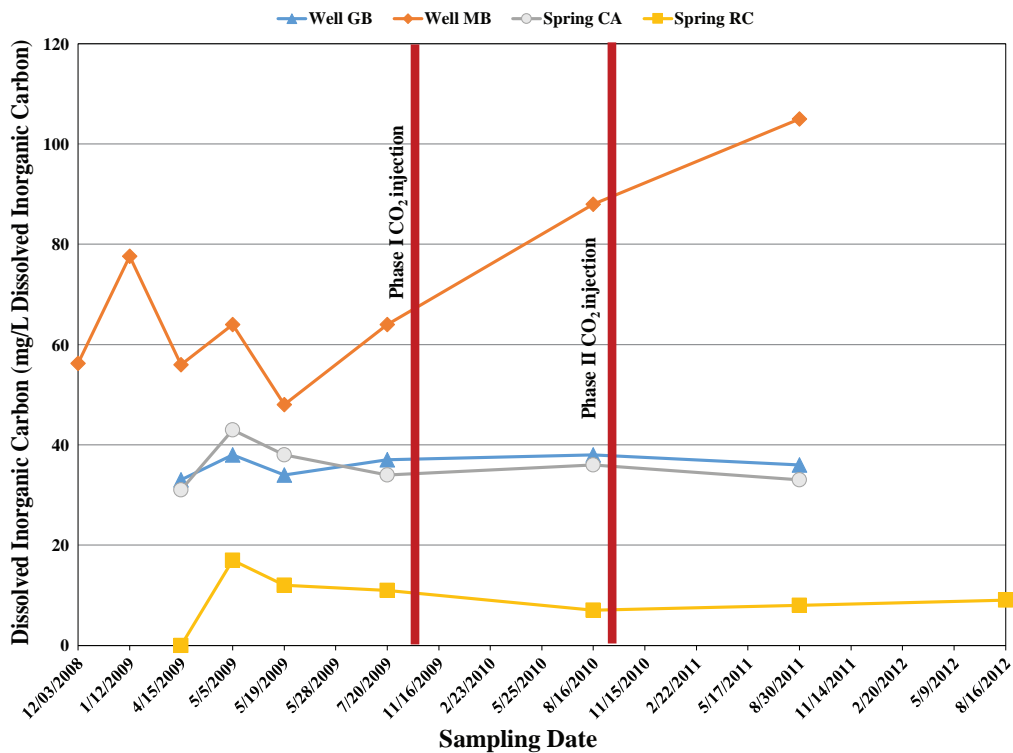


Figure 13. Dissolved inorganic carbon concentrations over time for wells GB and MB and springs CA and RC. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

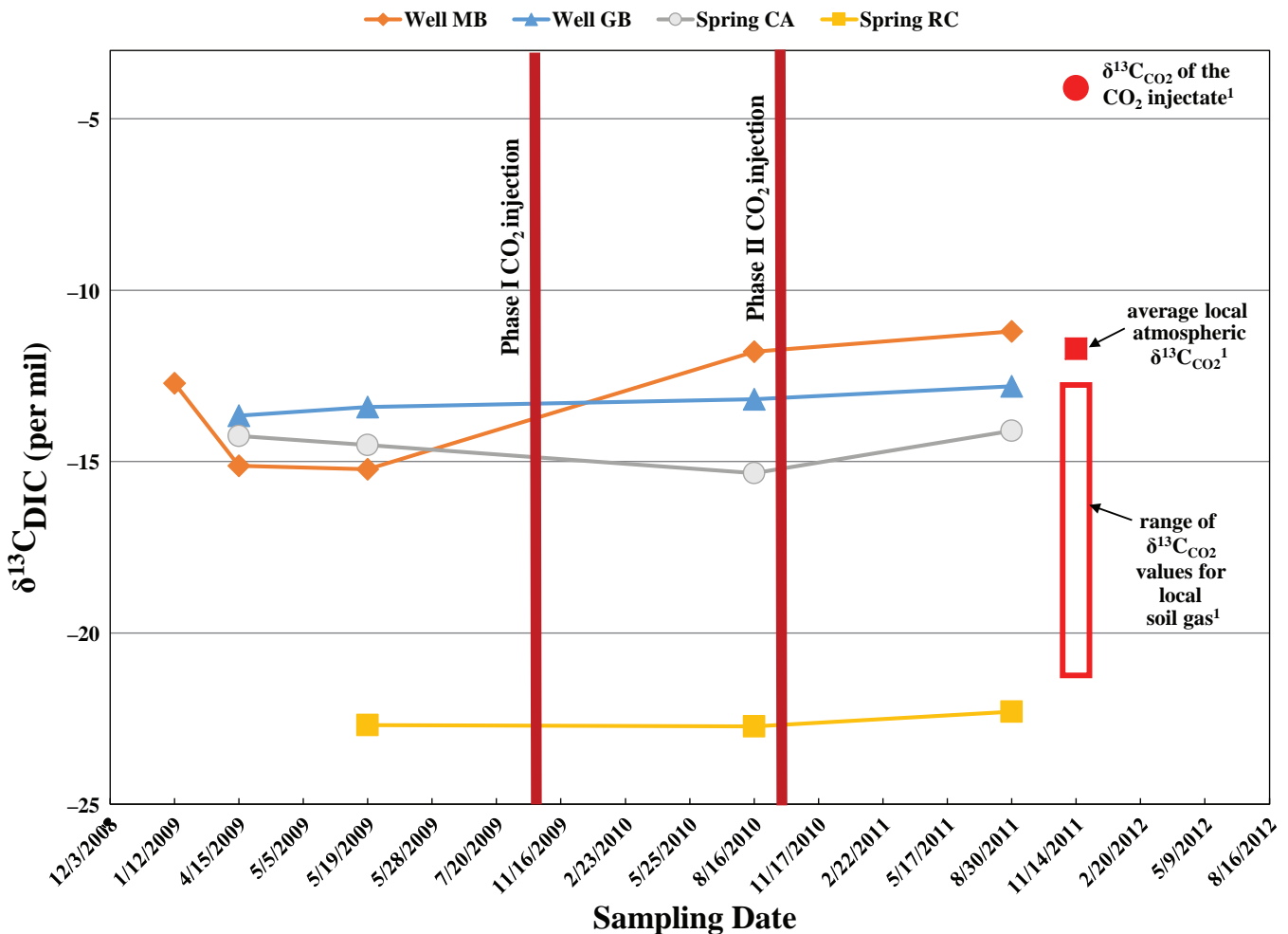


Figure 14. $\delta^{13}\text{C}_{\text{DIC}}$ values over time for wells GB and MB and springs CA and RC. Phase I CO_2 injection occurred August 18, 2009, and phase II CO_2 injection occurred September 22, 2010. ¹Unpublished data from Marty Parris (Kentucky Geological Survey, 2008).

of dissolved inorganic carbon. The less-enriched $\delta^{13}\text{C}_{\text{DIC}}$ values for all sites clearly indicate that injectate CO_2 did not migrate into the shallow groundwater aquifers in the area of the monitoring sites.

Total Dissolved Solids and Metals

Total dissolved solids is the concentration of all dissolved inorganic minerals in a water sample (Driscoll, 1986). Changes in TDS concentration can readily indicate the dissolution or precipitation of inorganic minerals in solution. For example, the injection of CO_2 into saline aquifers in Texas (Kharaka and others, 2006) and Kentucky (Frailey and others, 2012) caused dissolution of rock-forming carbonate and silicate minerals, and increased TDS concentrations. Smyth and others (2009) documented

the same outcome when CO_2 was introduced into a simulated freshwater aquifer. Where lower pH causes dissolution, laboratory and field tests have shown that reactions with carbonate minerals are typically faster than those with silicate minerals (Palandri and Kharaka, 2004).

TDS concentrations for the four monitoring sites ranged from less than 10 to 1,048 mg/L. The highest TDS concentrations (292–1,048 mg/L) were at well MB, whereas the lowest concentrations (less than 10–86 mg/L) were at spring RC (Fig. 15). TDS concentrations for well GB and spring CA were consistently around 200 mg/L.

TDS concentrations varied the most at well MB. Major metals concentrations, at all four sites, were fairly consistent over time, with the ex-

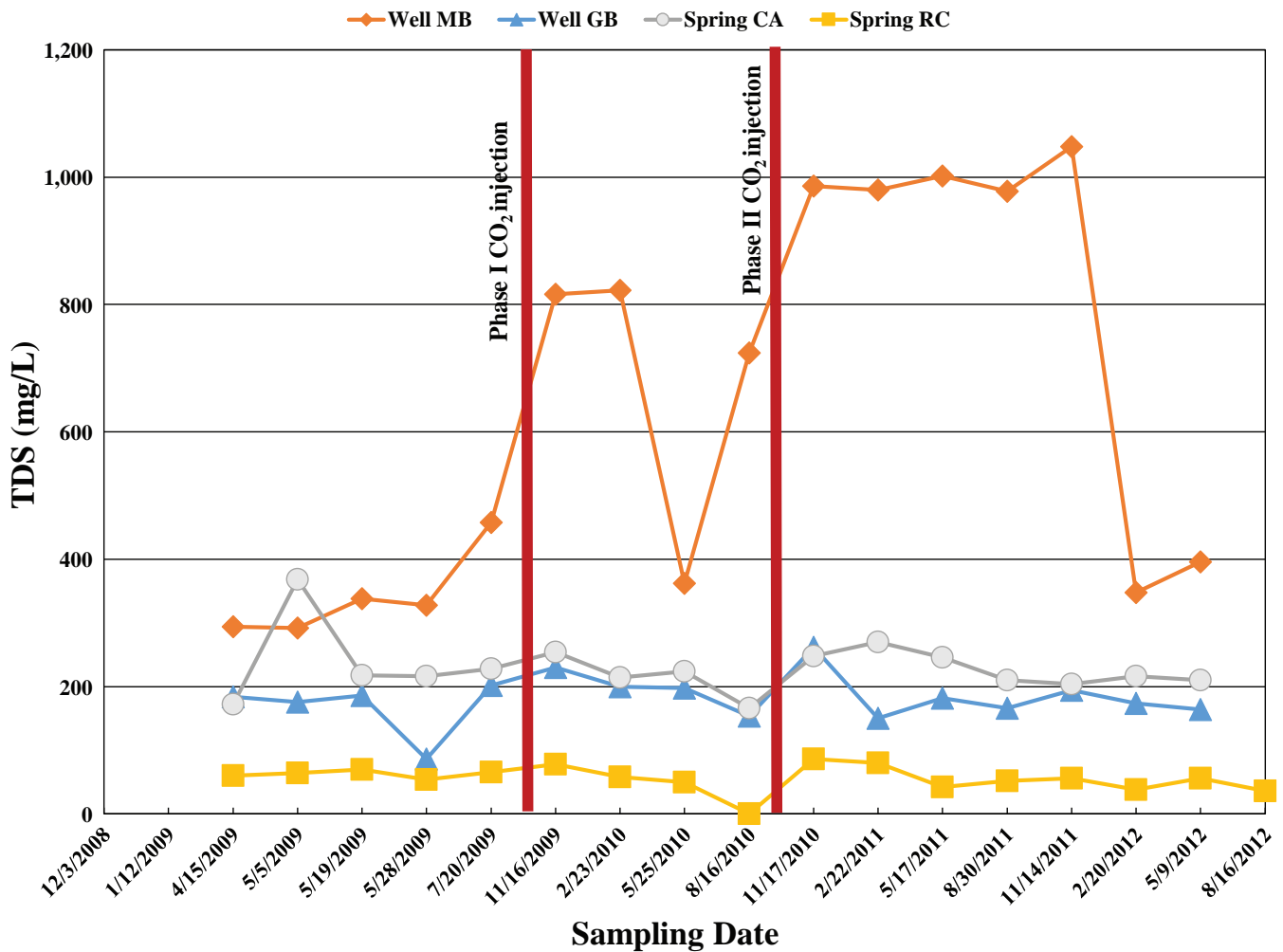


Figure 15. TDS concentration over time for wells GB and MB and springs CA and RC. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

ception of the sodium concentration at well MB (Table 11). Sodium at well MB is the only metal that increased in concentration over time (Fig. 16). The exact source of the increased sodium is not known, but is most likely associated with surface water leaking into well MB during or after precipitation. The elevated TDS concentrations in well MB samples are most likely associated with increases in bicarbonate, since TDS and bicarbonate graphs follow the same pattern over time (Figs. 11, 15). Other than the leakage influence at well MB, the relatively constant TDS and metals concentrations at the other sites suggest that no injectate CO₂ migrated into the shallow groundwater during the extent of this project.

Turbidity

Turbidity is a measurement of how much suspended mineral and organic particles are in a groundwater sample and can be used as an approximation of total suspended solids (Patzke, 2006). In this report, turbidity measurements are presented as nephelometric turbidity units. When sampling groundwater, especially with submersible pumps in wells, optimum turbidity is less than 10 NTU (Patzke, 2006). When using submersible pumps, elevated turbidity levels (greater than 10 NTU) may indicate that the pumping rate used to purge the well is too high, thereby creating turbid flow. Change in turbidity can also indicate a change in groundwater quality.

Table 11. Statistical summaries for the major metal concentrations from the four monitoring sites. The “<” sign indicates the analyte concentration was below the method detection limit. The concentration next to the “<” sign is the method detection limit. All concentrations are in mg/L.

Site	Statistic	Al	Ba	Be	Ca	Fe	Mg	Mn	K	Si	Na	Sr
MB	n	8	8	8	8	8	8	8	8	8	8	8
	minimum		0.020		5	< 0.002	1.9	< 0.001	1.2	3.4	12.7	0.08
	mean		0.036		44	0.019	10.4	0.034	3.1	4.0	154.4	0.19
	maximum	< 0.061	0.050	< 0.001	77	0.080	15.1	0.050	4.7	5.0	445.0	0.28
	standard deviation		0.011		26	0.028	4.5	0.040	1.3	0.5	150.1	0.07
GB	n	6	6	6	6	6	6	6	6	6	6	6
	minimum		0.007		49	0.003	5.6	0.001	0.4	6.7	6.4	0.08
	mean		0.009		53	0.010	5.9	0.007	0.5	7.2	6.8	0.09
	maximum	< 0.061	0.010	< 0.001	59	0.030	6.1	0.020	0.6	7.3	7.2	0.09
	standard deviation		0.001		4	0.010	0.2	0.007	0.1	0.2	0.3	0.01
CA	n	6	6	6	6	6	6	6	6	6	6	6
	minimum		0.030		46	< 0.002	5.5	0.002	0.7	5.5	7.8	0.12
	mean		0.035		54	0.001	6.3	0.005	1.0	6.5	11.1	0.14
	maximum	< 0.061	0.040	< 0.001	58	0.004	7.4	0.009	1.2	7.2	15.4	0.15
	standard deviation		0.006		5	0.002	0.7	0.003	0.1	0.7	2.5	0.01
RC	n	7	7	7	7	7	7	7	7	7	7	7
	minimum		0.005		3	< 0.002	1.5	0.002	0.3	9.2	5.6	0.01
	mean		0.007		3	0.004	1.5	0.006	0.4	9.9	6.3	0.01
	maximum	< 0.061	0.010	< 0.001	3	0.010	1.5	0.009	0.5	10.5	6.9	0.02
	standard deviation		0.002		0	0.003	0.03	0.002	0.1	0.6	0.5	0

Groundwater turbidity values at the four monitoring sites ranged from less than 0.1 to 322 NTU. Of the 63 turbidity measurements analyzed, 86 percent were less than 10 NTU. The highest values were in samples collected from well GB (Fig. 17). Bicarbonate and TDS concentrations (Figs. 11, 15) and pH values (Fig. 10) for samples collected from well GB were consistent throughout the monitoring period, which indicates that the elevated turbidity was not associated with any groundwater quality changes. Elevated turbidity values at well GB can most likely be attributed to the existing domestic submersible pump creating turbid flow during the sampling process. For example, while sampling well GB on 5/17/2011, the water was very turbid and had an iron red color, resulting in the highest turbidity value (322 NTU) at any of the four monitoring sites (Fig. 17).

Conclusions

Groundwater-quality data collected from two domestic wells and two domestic springs

were used to determine if CO₂ injected into deep saline aquifers migrated into shallow aquifers within a 2-mi radius of the injection site. pH values at the four monitoring sites ranged between 4.58 and 7.82. All sites exhibited a pH variation of about 1 pH unit throughout the sampling period, and there were no decreases in pH over time after CO₂ injection occurred. The lack of a decrease in pH suggests that CO₂ injectate did not migrate into the shallow groundwater system. With the exception of well MB, bicarbonate, total CO₂, dissolved inorganic carbon, and TDS concentrations varied little over time. Therefore, any changes in concentration related to the presence of injectate in the groundwater at these sites should have been detected. Higher variations in bicarbonate, total CO₂, dissolved inorganic carbon, and TDS concentration in well MB were attributed to well leakage caused by improper well construction. δ¹³C_{DIC} values confirmed that injectate was not present in the aquifer at well MB. Therefore, because of potential natural background variations, especially when

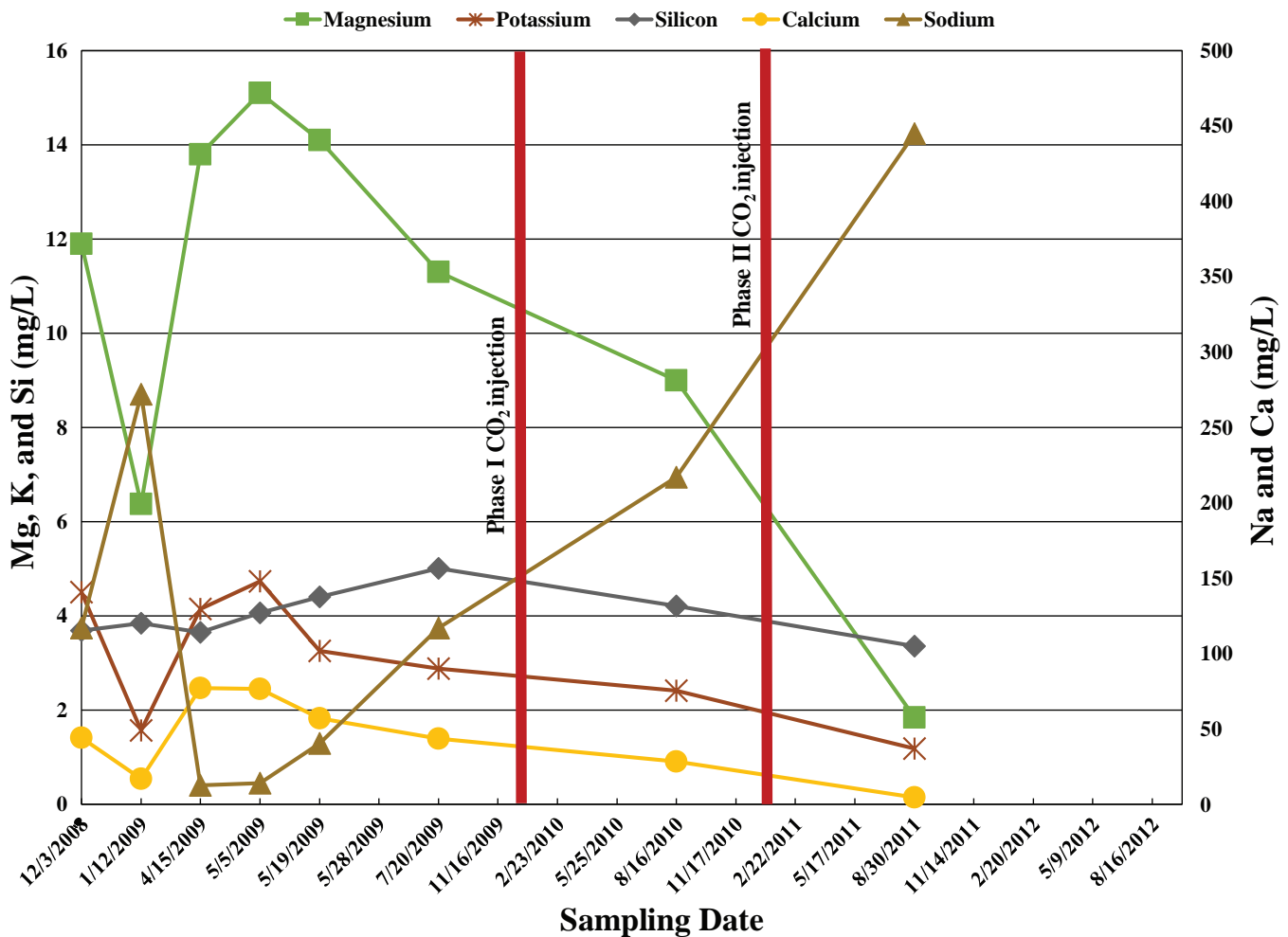


Figure 16. Magnesium, potassium, silicon, calcium, and sodium concentrations over time at well MB. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

well construction integrity is questionable, $\delta^{13}\text{C}_{\text{DIC}}$ should be included in the sampling protocol when attempting to determine the presence of CO₂ injectate in groundwater systems. Therefore, groundwater-quality data collected from two domestic wells and two domestic springs suggest that CO₂ injected below a depth of 3,570 ft had not migrated vertically into the four monitored aquifers before sampling was discontinued.

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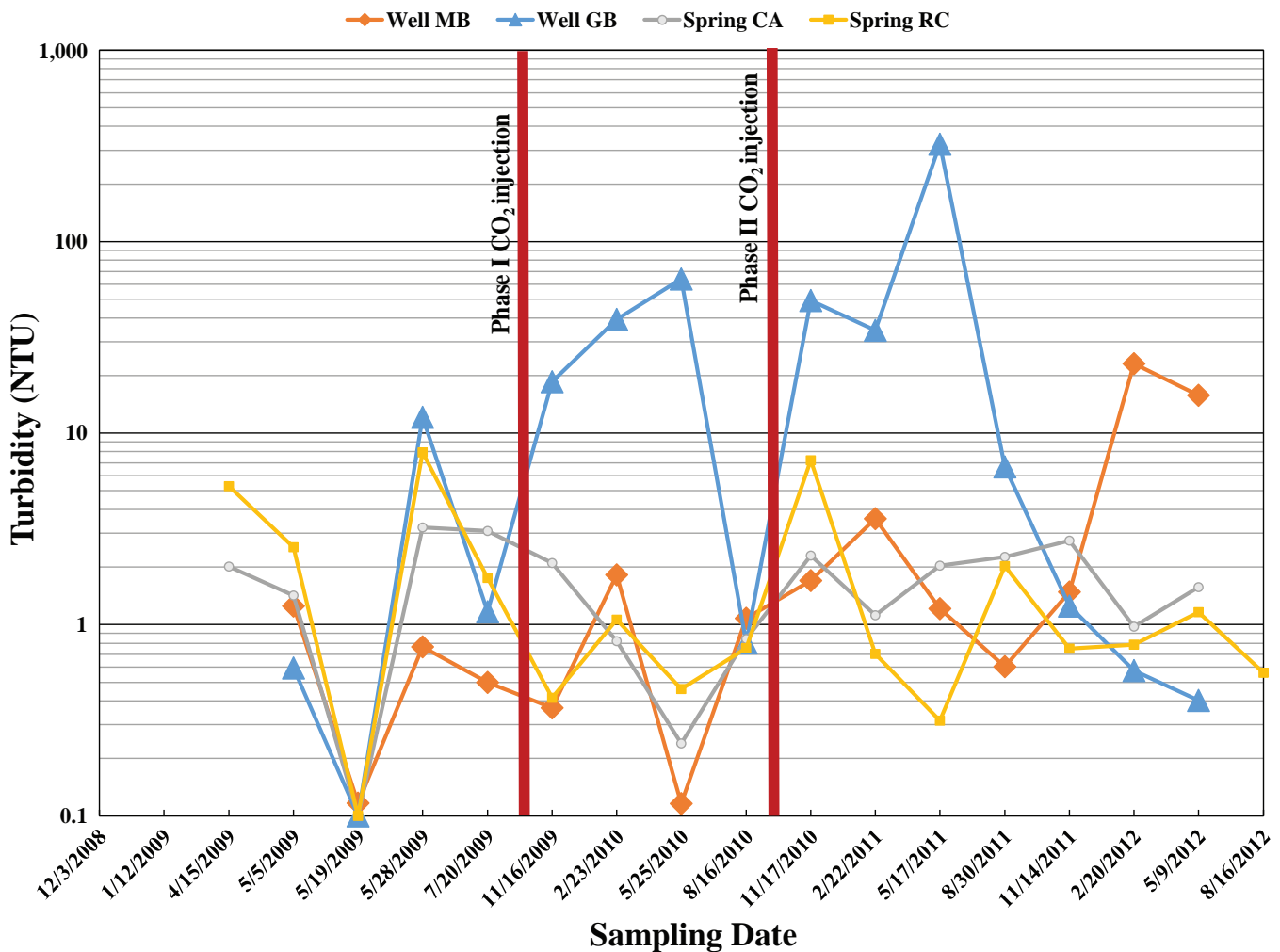


Figure 17. Turbidity values for samples from the monitoring sites. Phase I CO₂ injection occurred August 18, 2009, and phase II CO₂ injection occurred September 22, 2010.

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