2015

The environmental effects of geologically sequestered carbon dioxide gas and the enhanced recovery of coal bed methane from an unmineable coal seam

Brad David Hega

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Hega, Brad David, "The environmental effects of geologically sequestered carbon dioxide gas and the enhanced recovery of coal bed methane from an unmineable coal seam" (2015). *Graduate Theses, Dissertations, and Problem Reports*. 5789.

<https://researchrepository.wvu.edu/etd/5789>

This Thesis is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Thesis has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

THE ENVIRONMENTAL EFFECTS OF GEOLOGICALLY SEQUESTERED CARBON
DIOXIDE GAS AND THE ENHANCED RECOVERY OF COAL BED METHANE FROM
AN UNMINEABLE COAL SEAM

Brad David Hega

Thesis submitted to:
The Eberly College of Arts and Sciences
West Virginia University

In partial fulfillment of the requirements for the degree of

Master of Science in

Geology

Committee

Henry W. Rauch, PhD – Chair
Thomas H. Wilson, PhD
James E. Locke, CONSOL Energy Inc.

Department of Geology and Geography

Morgantown, WV
2014

Keywords: Carbon dioxide, environmental, sequestration, methane, geochemistry, ZERT

Copyright 2015: Brad D. Hega

Abstract

THE ENVIRONMENTAL EFFECTS OF GEOLOGICALLY SEQUESTERED CARBON DIOXIDE GAS AND THE ENHANCED RECOVERY OF COAL BED METHANE FROM AN UNMINEABLE COAL SEAM

Brad D. Hega

The need to mitigate the alleged effects of anthropogenic carbon dioxide gas ($\text{CO}_{2(g)}$) generation has led to the exploring of specific subsurface environments to house the gas. The geology of the subsurface underlying Marshall County West Virginia makes the area an ideal setting for use as a $\text{CO}_{2(g)}$ repository. A cooperative, pilot study was undertaken by CONSOL Energy Inc., which owns and operates the selected $\text{CO}_{2(g)}$ sequestration site, along with personnel from West Virginia University (WVU) and other agencies under the United States Department of Energy (DOE) funded Zero Emissions Research Technology or ZERT program. The repository is an unmineable coal bed/seam overlain predominantly by shale. A potential residual effect of the geologic sequestration of $\text{CO}_{2(g)}$ is the enhanced recovery of otherwise unrecoverable coal bed methane gas ($\text{CH}_{4(g)}$). The environmental effects of this type of geologic $\text{CO}_{2(g)}$ sequestration were previously unknown. Here we demonstrate methods of monitoring and any potential signatures of $\text{CO}_{2(g)}$ on the ground water, surface water, soil zone, and head space gases as well as the migration of perfluorocarbon (PFC) tracer, injected and tested by National Energy Technology Laboratory (NETL) researchers, within a 1 kilometer (km) square test grid where $\text{CO}_{2(g)}$ and $\text{CH}_{4(g)}$ related activities are taking place. The findings indicate the possibility of the microseepage of injected $\text{CO}_{2(g)}$ within the soil zone; the possibility of slight $\text{CO}_{2(g)}$ chemical weathering within the aquifer underlying the center of the test site square; an injected $\text{CO}_{2(g)}$ exacerbated head space $\text{CH}_{4(g)}$ pollution event; and a failure of the cement plug at the base of access well MH-19. The secondary findings indicate two separate coal bed formation (residual brine) water pollution events, affecting two test site ground water wells and two stream sampling locations; one event was accidental, while the other event is alleged to be intentional. The environmental effects of geologically sequestered $\text{CO}_{2(g)}$ may not be fully understood at the $\text{CO}_{2(g)}$ injection site, considering the lack of long periods of sustained $\text{CO}_{2(g)}$ injection and the lack of $\text{CO}_{2(g)}$ injection during the biologically dormant (winter) seasons during the study period.

Acknowledgements

I am very grateful for being given the opportunity to work on such a prestigious research project through West Virginia University. I would like to sincerely thank Dr. Henry Rauch for the amazing learning experience, providing support, and helping me in every way possible. I would also like to extend a special thank you to Dr. Richard Bajura for providing the funding necessary to ensure the success of the research project.

The research project could not have been possible without the funding provided by DOE-NETL, NRCCE, and NSF. I am appreciative of CONSOL Energy Inc. for providing the land area for research and for granting access to the research site. I would like to extend a heartfelt thank you to James Locke and Richard Winschel of CONSOL Energy Inc. for providing the funding for water sample chemical analysis and also for the laboratory support received. I would like to extend my gratitude to Arthur Wells, J. Rodney Diehl, and Dennis Stanko of DOE-NETL for providing PFC tracer data. The success of the research project would not have been possible without my dedicated field assistants; Gayle Harman, Stacy Berry, Katherine Felton, Brandt Rouse, Steve Henry, and Chris Smith. It was sincerely a pleasure to work with all of you.

Finally and most importantly I would like to thank my wife Lori and my sons Mason and Logan for their support and tolerance during this latest adventure; I love the three of you more than you will ever know.

Table of Contents

List of Figures.....	iii
List of Tables	ix
Introduction.....	1
Methods.....	6
Water.....	6
Head Space Gases.....	15
Perfluorocarbon Tracers	18
Discussion and Results.....	19
Domestic Water Supplies.....	19
Test Site Waters.....	22
Test Site Surface Water	23
Test Site Ground Water	36
Soil Zone Head Space CO ₂ Gas	63
Isotope Data Analysis of Bethany Meier	70
Water Well Head Space CO ₂ Gas	75
Perfluorocarbon Tracers.....	79
Conclusions.....	88
Stream Water Chemistry.....	88
Natural Ground Water Chemistry	88
Contaminated Ground Water Chemistry	90
Vadose Zone CO ₂ Chemistry.....	92
Perfluorocarbon Tracer Interpretation	93

Overall Findings.....	94
References	95

List of Figures

Figure 1: Geologic map of West Virginia with the location of the CONSOL-ZERT Marshall County field test site indicated by the callout at the top left.....	2
Figure 2: The surface site of the CO _{2(g)} sequestration and ECBM pilot recovery project; the area of interest is outlined by the coal bed CH _{4(g)} production laterals (dark pink lines) forming the square shape.....	3
Figure 3: Schematic scheme of the CONSOL-ZERT Marshall County test site detailing the target coal beds for carbon dioxide gas storage and enhanced coal bed methane gas recovery. The Pittsburgh coal bed and the Upper Freeport coal bed are ~600 feet and ~1250 feet deep below valley bottom respectively. CO _{2(g)} is only being injected into the Upper Freeport coal bed.....	4
Figure 4: The CONSOL-ZERT Marshall County pilot carbon dioxide sequestration/enhanced coal bed methane recovery test site showing the UTM grid and the hydrogeologically significant monitoring points/locations.....	5
Figure 5: Cross section of test site ground water monitoring well W-2. The green interval represents the plastic screen liner. The other two monitoring wells, W-1 and W-3, are constructed identically, except for well W-3 where the water table is situated below the casing bottom which exposes the lower vadose zone to the well.....	7
Figure 6: A typical test site shallow soil zone monitoring well, general soil composition of the area and soil depth range.....	17
Figure 7: Average monthly stream discharge through time. The highest discharge values occur during the wet (winter through spring) seasons.....	24
Figure 8: Average monthly test site stream water field measured pH through time. The blue arrow indicates the pre CO ₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO ₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO ₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO ₂ gas injection.....	25
Figure 9: Average monthly test site stream water field measured electrical conductance through time. The blue arrow indicates the pre CO ₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO ₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO ₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO ₂ gas injection.....	26

Figure 10: Average monthly test site stream water dissolved $\text{CO}_{2(\text{aq})}$ concentrations based on chemical equilibria, $\text{PCO}_{2(\text{aq})}$, and field pH through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....27

Figure 11: Average monthly test site stream water dissolved cation concentrations at sampling point S-1 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....28

Figure 12: Average monthly test site stream water total anion concentrations at sampling point S-1 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....29

Figure 13: Average monthly test site stream water dissolved cation concentrations at sampling point S-2 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....30

Figure 14: Average monthly test site stream water total anion concentrations at sampling point S-2 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....31

Figure 15: Average monthly test site stream water dissolved cation concentrations at sampling point S-3 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....32

Figure 16: Average monthly test site stream water total anion concentrations at sampling point S-3 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.....33

Figure 17: Map view of the area on July 26, 2007; this became the center of the test site square and where the $\text{CO}_{2(\text{g})}$ injection system is located via UTM meter grid values.....35

Figure 18: Average monthly test site ground water field measured pH through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....38

Figure 19: Average monthly test site ground water field measured electrical conductance through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....39

Figure 20: Average monthly dissolved CO_{2(aq)} concentrations through time, based on test site ground water chemical concentrations, chemical equilibria, PCO_{2(aq)}, and field pH through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....41

Figure 21: Average monthly dissolved cation concentrations for test site ground water at well sampling well W-1 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....42

Figure 22: Average monthly test site ground water total anion concentrations at well sampling point W-1 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....43

Figure 23: Potential point source of brine pollution from coal bed formation water. Brine water has been observed emanating from the area of the MH-12 CH_{4(g)} production well pump jack, where the polished rod enters the casing head; note the wet, iron stained ground, which has since been covered with fresh limestone gravel.....46

Figure 24: Average monthly test site ground water dissolved cation concentrations at ground water well sampling point W-2 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....47

Figure 25: Average monthly test site ground water total anion concentrations at ground water well sampling point W-2 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....48

Figure 26: Determination and correlation coefficients (R^2 and R respectively) of the down bore pressure of CO_{2(g)} injection well MH-18 versus the field measured electrical conductance of the ground water from test site well W-2. The R value is significant at 0.01 α ; the R^2 value shows 46.7% of the data can be attributed to the regression trend based on a 29 months lag.....50

Figure 27: Average monthly test site ground water dissolved cation concentrations at ground water well sampling point W-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....51

Figure 28: Average monthly test site ground water total anion concentrations at ground water well sampling point W-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.....52

Figure 29: The volume percent concentration of CH_{4(g)} in the head space of well W-3 through time. The data collected by CONSOL Energy Inc. personal are indicated by large black squares; the rest of the data were collected by WVU personnel.....54

Figure 30: Schoeller diagrams of the geochemical signatures typical of coal bed formation waters within CH_{4(g)} bearing coal seams. Graph f represents the geochemical signature of the ground water extracted from well W-3.....56

Figure 31: Data plot for test site ground water monitoring well W-3 showing the monthly average values of HCO₃^{1-(aq)} concentration and ground water calcite saturation index through time.....59

Figure 32: Location of deep monitoring bores MH-26 and MH-27 relative to shallow ground water monitoring well W-3.....60

Figure 33: Cross section of deep monitoring bore MH-26 in relation to ground water monitoring well W-3 and shallow vadose zone monitoring well W-3A moving from east (left side) to west (right side). The red interval at well W-3 is the open screened length of the borehole while the blue interval represents the cased length of the borehole. The blue line with upside down triangles represents the water table and red line with upside down triangles shows the approximate position of the fresh water/brine water interface.....61

Figure 34: Monthly average head space CO _{2(g)} concentrations through time. Shallow soil zone monitoring wells W-2A, W-2D, W-3A, and W-6 are within the confines of the test site square, while W1A and W-4/4A are on/near the boundaries of the test site square. The control wells are W-5 and W-7, which are east and west of the test site square respectively.....	64
Figure 35: Monthly average head space CO _{2(g)} concentrations in wells W-2A and W-5 vs. the CO _{2(g)} injection bore gauge pressures in wells MH-18 and MH-20 through time.....	66
Figure 36: Determination and correlation coefficients (R ² and R respectively) of pounds per square inch at the gauge (psig) of CO _{2(g)} injected into well MH-18 versus the average head space CO _{2(g)} concentration of shallow soil zone head space gas in monitoring well W-2D. The R value is significant at 0.01α; the R ² value shows 57.5% of the data can be attributed to the regression trend based on a 12 month lag for prior CO _{2(g)} injection pressure.....	69
Figure 37: Determination and correlation coefficients (R ² and R respectively) of pounds per square inch at the gauge (psig) of CO _{2(g)} injected into well MH-20 versus the average head space CO _{2(g)} concentration of shallow soil zone head space gas in monitoring well W-2D. The R value is significant at 0.01α; the R ² value shows 59% of the data can be attributed to the regression trend based on a 12 month lag for prior CO _{2(g)} injection pressure.....	70
Figure 38: Close up of a shallow soil zone gas monitoring well. A septum fitted vial is placed on the hypodermic needle, which is connected to a length of plastic tubing in order to collect a head space gas sample via diffusion.....	71
Figure 39: Average head space CO _{2(g)} concentrations incorporating all data points in each active shallow soil zone monitoring during the study period. Horizontal distance is not to scale..	73
Figure 40: Aerial view of the Marshall county test site and the locations of the shallow soil zone monitoring wells; the center, and eastern and western boundaries of the test site square; and the average (of all collected data) for shallow soil zone CO _{2(g)} % volume concentrations.....	74
Figure 41: Monthly average head space CO _{2(g)} concentrations in shallow ground water monitoring wells W-1, W-2, and W-3 vs. the CO _{2(g)} injection bore gauge pressures of MH-18 and MH-20 through time.....	76
Figure 42: Cross section of test site ground water monitoring well W-3 where the water table is situated below the casing bottom which exposes gases of the lower vadose zone to the well. The green interval represents the plastic screen liner.....	78
Figure 43: PTCH and PMCH tracer detection at production wells MH-11 and MH-12 at the number of days from the start of tracer injection.....	80
Figure 44: Map view of the center of the test site square and where the CO _{2(g)} injection system is located.....	83

Figure 45: Cross sectional view of the subsurface facing north. The schematic is a representation of the suspected avenues of leakage of PTCH tracer into the PCB 500 feet to 600 feet above the repository UFCB. A' red vertical to the horizontal transition was the first and second cement plugging attempts of MH-19, the green offshoot from A' was the third cement plugging attempt of MH-19, and A^O was the fourth and final cement plugging attempt of MH-19.....84

List of Tables

Table 1: The lithology of each of the three, W-1, W-2, and W-3, test site shallow ground water monitoring wells.....	8
Table 2: Known specifications of domestic supply water sources; these sources are used as controls for the general water chemistry of the area around the research site.....	11
Table 3: Average values for select domestic supply water parameters across the study.....	19
Table 4: Average values for dissolved cations in domestic supply water across the study.....	19
Table 5: Average values for total anions in domestic supply water across the study.....	19
Table 6: Average values for select stream water parameters across the study period.....	23
Table 7: Average values for dissolved cations in stream water across the study period.....	23
Table 8: Average values for total anions in stream water across the study period.....	24
Table 9: Average values for select test site ground water parameters across the study period.....	36
Table 10: Average values for dissolved cations in test site ground water across the study period.....	36
Table 11: Average values for total anions in test site ground water across the study period.....	37
Table 12: The differences among average electrical conductivity values from background of the ground water from test site well W-2 during different phases of CO _{2(g)} injection activity; note the period during automated injection has the highest positive difference.....	40
Table 13: Average CH _{4(g)} volume percent concentration in the head space of each test site shallow ground water monitoring well across the CH _{4(g)} data collection period.....	45
Table 14: Average of the monthly average values of HCO ₃ ¹⁻ _(aq) concentrations in ground water wells and the percent of the HCO ₃ ¹⁻ _(aq) value observed in well W-3.....	57
Table 15: Average monthly CO _{2(g)} concentrations, in volume percent units, of shallow soil zone monitoring wells W-2A and W-2D, located in the center of the test site square, and shallow soil zone monitoring control well W-5, located ~1.0 miles SSE from the center of the test site square.....	67

Table 16: Growing season average head space CO_{2(g)} concentrations in wells W-1, W-2, and W-3 and the percent head space CO_{2(g)} concentration increase from background during subsequent growing seasons.....77

Table 17: Regression analysis based on mass of CO_{2(g)} injected with the CO_{2(g)} injection lag time where the R value is most significant at 0.01 α . The R² value indicates the correlation percentage of the data attributed to the regression trend.....81

Table 18: Regression analysis based on CO_{2(g)} injection pressure with CO_{2(g)} injection lag time where the R value is most significant at 0.01 α . The R² value indicates the correlation percentage of the data attributed to the regression trend81

Introduction

The CONSOL Energy Inc. carbon capture and storage/enhanced coal bed methane (CCS/ECBM) recovery test site (CNX Georgetown) is located on a bench in the southeast flank of the Washington anticline in Marshall County, West Virginia (Figure 1) along the former Baltimore & Ohio (B&O) Railroad line along the southern bank of the Pennsylvania Fork of Fish Creek (the stream). The test site is between the towns of Georgetown, WV to the east and Bellton, WV to the west. The cooperating agencies performed specific tasks during the pilot study. CONSOL Energy Inc., through ZERT, was the lead agency for the Marshall County CO_{2(g)} sequestration site and was also responsible for the monitoring of coal bed formation water and gas content. DOE NETL monitored for potential surface microseepage and subsurface migration of sequestered CO_{2(g)}. The WVU Department of Geology and Geography was responsible for geophysical characterization of the subsurface underlying the research site as well as the environmental monitoring of shallow ground water and surface water, head space CO_{2(g)} and CH_{4(g)} concentrations of the ground water monitoring wells and shallow soil zone monitoring wells. The WVU College of Engineering and Mineral Resources was responsible for the monitoring of ground movement as well as other activities related to the subsurface.

Figure 1: Geologic map of West Virginia with the location of the CONSOL-ZERT Marshall County field test site indicated by the callout at the top left (base map courtesy of the West Virginia Geological and Economic Survey).

The test site is a one kilometer grid encompassing a portion of the hilltops and valley associated with the stream. Figure 2 depicts the outline of the test site and the various points associated with (CO_{2(g)}) injection and ECBM recovery, at the center and top and bottom corners respectively.

Figure 2: The surface site of the $\text{CO}_{2(g)}$ sequestration and ECBM pilot recovery project; the area of interest is outlined by the coal bed $\text{CH}_{4(g)}$ production laterals (dark pink lines) forming the square shape (courtesy of Hema J. Siriwardane, West Virginia University).

The Pennsylvania Fork of Fish Creek is a tributary of the Ohio River and, over geologic time, has formed a deep valley exposing rock strata of Permian age. The strata of the area consist of alternating beds of sandstone, silt/mud/claystone, limestone, coal beds (major and minor), and shale (Hennen and White, 1909); a deep seated unminable coal bed and the overlying major shale units make this area geologically attractive for the sequestration of $\text{CO}_{2(g)}$ and enhanced coal bed methane production.

The stream's horseshoe meander bend dissects the test site topography with the cut bank being associated with the steep terrain on the north side of the meander. The strata from the hilltops to a depth of ~560 feet below said hilltops have a general strike in the northeast direction, a general dip of 2-5° west, are Permian in age, and are part of the Dunkard Group, Greene, Washington, and Waynesburg Formations (Hennen and White, 1909). The target coal bed for

CO_{2(g)} sequestration is the Pennsylvanian age Upper Freeport coal bed (UFCB) seated ~1250 feet below the stream valley surface and is unminable in this particular region. The coal bed undergoing the majority of the ECBM recovery is the Pennsylvanian age Pittsburgh coal bed (PCB) seated ~600 feet below the stream valley bottom and is minable in the region. Figure 3 represents a generalized schematic example of the subsurface system.

Figure 3: Schematic scheme of the CONSOL-ZERT Marshall County test site detailing the target coal beds for carbon dioxide gas storage and enhanced coal bed methane gas recovery (courtesy of CONSOL Energy, Inc.). The Pittsburgh coal bed and the Upper Freeport coal bed are ~600 feet and ~1250 feet deep below valley bottom respectively. CO_{2(g)} is only being injected into the Upper Freeport coal bed.

The subsurface lithology below ~560 feet from the hilltops exhibits a south and east dip of ~2° or less (Winschel et al., 2010). The PCB is a unit at the base of the Pittsburgh Formation of the Monongahela Group, while the UFCB is a unit at the base of the Glenshaw Formation of the Allegheny Group (Hennen and White, 1909); other groups and their associated formations are present between the strata of concern for this particular study. Strategic locations for monitoring points were selected within the test site perimeter based on topography, drainage

patterns/local drainage basins, speculated fractures/fracture zones, and the geology/stratigraphy of the area. Five domestic supply water wells and one domestic supply fresh water spring were chosen as potential controls based on proximity to the research site via up/down stream locations. Figure 4 is a site map showing the monitoring points/locations associated with the hydrogeological and soil gas research for this particular pilot CCS/ECBM recovery study.

Figure 4: The CONSOL-ZERT Marshall County pilot carbon dioxide sequestration/enhanced coal bed methane recovery test site showing the UTM grid and the hydrogeologically significant monitoring points/locations (adapted from Thomas Wilson, West Virginia University).

Methods

Water: Cato Drilling LLC of Morgantown, West Virginia drilled and installed the shallow ground water monitoring wells W-1, W-2, and W-3 at the research site in early May 2008. Although the driller was present during the well location selection process, he failed to notify the researchers he was beginning well installation and mistook a similar orange stake east of where well W-3 was to be located (near soil gas well W-4/4A in Figure 4), and drilled and installed well W-3 there. No further mistakes were made as the driller notified the researchers of his activities after completion of well W-3, but prior to the installation of the other wells, W-1 and W-2.

Figure 5 shows the details of the well design in cross section. The test site shallow ground monitoring wells were drilled to a depth of 105 feet through alternating beds of sandstone and shale with varying thicknesses encountered at each location. A 6 inch diameter borehole was drilled from the ground surface to a depth of ~20 feet to accommodate the well casing and annulus zone grouting. The borehole has a diameter of 5 inches, from a depth of ~20 feet to 105 feet below the ground surface, to accommodate the screened and lined intervals. The screened interval extends from 100 feet to 40 feet below the ground surface and has an open bottom with the remaining upper 40 feet constituting the lined interval. The screen and liner are 4 inch diameter, schedule 40 polyvinylchloride (PVC) pipe while the casing is 5 inch diameter, schedule 40 PVC pipe and has a total length of ~21.5 feet with ~1.5 feet protruding above the ground surface. Each section of screen and liner are 20 feet long and are joined via fixed bell connectors using PVC plumbing glue. The annulus zone is grouted, in the 6 inch borehole that houses the casing, with sodium bentonite flakes/crumbles from a depth of 20 feet to the ground surface.

Diagram illustrating the cross-section of monitoring well W-1 and W-2. The well is installed in a borehole with a diameter of 5.75 in (14.6 cm) OD and 5.25 in (13.3 cm) ID. The casing has an outer diameter (OD) of 5.25 in (13.3 cm) and an inner diameter (ID) of 4.75 in (12.1 cm). The well is surrounded by bentonite clay. The well is located in a soil and fill area, with the average water table depth indicated by a blue line. The well extends to a depth of 105 ft (32 m) below the ground surface, where it terminates in a screened section. The well is labeled "Monitoring well W-1 and W-2".

The casing and grout penetrated into the bedrock thus ensuring minimal natural vadose gas exchange with the ground water monitoring wells. The caps used for the three wells have morphed over time into a final design that is air tight, but allows for in situ as well as syringe and evacuation monitoring of the gases that accumulate in the head space of the wells. The ground water is extracted via a dedicated stainless steel Schaefer Legacy 240 volt electric water pump rated at 10 gallons per minute (gpm), which is set ~8 feet from the bottom of each well.

7

varies from course grained sandstone at W-1, fining down westward to sandy shale at W-3; the aquifer at W-2 is fine grained sandstone with shale streaks. Table 1 below shows the depth (from ground surface), thickness, and type of the lithology composing each shallow ground water monitoring well.

W-1			W-2		
To depth (ft)	Thickness (ft)	Rock strata	To depth (ft)	Thickness (ft)	Rock strata
14	14	fill soil/soil/overburden	7.5	7.5	soil/overburden
18	4	gray shale	17.5	10	gray sandstone, course
19.5	1.5	gray limestone	21	3.5	gray shale, soft
21	1.5	gray shale	24	3	gray limestone
30	9	gray sandstone, course	26	2	light gray shale/black shale
32	2	dark gray shale	61	35	gray sandstone with shale streaks
53	21	gray sandstone, course	62	1	gray limestone, soft
56	3	light gray shale	105	43	gray shale with streaks of red
57	1	dark gray sandy shale	W-3		
61	4	very dark shale	To depth (ft)	Thickness (ft)	Rock strata
69	8	red shale	3	3	fill/railroad bed
79	10	dark gray shale	48	45	gray shale
80	1	gray limestone	51	3	limestone
89	9	gray shale	74	23	sandy shale, green, massive
90	1	black shale	105	31	gray sandstone
92	2	dark gray shale	The stratigraphy of W-1 and W-2 are based on data collected by the researcher, while the stratigraphy of W-3 is based solely on the driller's log		
94	2	gray shale			
95	1	light gray shale			
97	2	gray sandstone, fine			
100	3	gray sandy shale			
103	3	gray limestone			
103.5	0.5	gray shale			
105	1.5	gray limestone			

Table 1: The lithology of each of the three, W-1, W-2, and W-3, test site shallow ground water monitoring wells.

Ground water monitoring well W-1 (Figure 4 above) is located ~2150 feet SSE from the center of the test site square and ~300 feet NE from the SE CH_{4(g)} production lateral pump jacks for wells MH-11 (UFCB) and MH-12 (PCB). The aquifer well W-1 penetrates a highly permeable coarse grained sandstone and is confined due to the low permeability shale layers at the top and base of the aquifer and the high position of the water table (potentiometric surface). Well W-1 reaches static equilibrium within 45 minutes at a pumping rate of 12 gallons per minute (gpm); the total drawdown is ~0.8 feet. The transmissivity (T) and hydraulic

conductivity (K) were determined using the Cooper-Jacob straight line method for confined aquifers (Fetter, 2001):

$$T = \frac{2.3Q}{4\pi\Delta(h_o - h)} \text{ AND } K = \frac{T}{b} \quad (1)$$

Where: Q = pumping rate (ft³/d units)

$\Delta(h_o - h)$ = the drawdown per log cycle of time (ft units)

b = aquifer saturated thickness (ft units)

The physical values of well W-1 were determined to be: transmissivity 617 ft²/d and hydraulic conductivity 8.8 ft/d. The results of the aquifer pump test at this location are reasonable, given relatively fast flow through a coarse grained sandstone.

Ground water monitoring well W-2 (Figure 4 above) is located ~218 feet N of the CO_{2(g)} injection structure along the 100 year flood plain on the southern side of the stream and is in the center of the test site square. The water-bearing stratum is a low permeability, fine grain sandstone with shale streaks and is capped by shale; well W-2 will pump dry in six to nine minutes at a pumping rate of ~12 gpm. The transmissivity (T) and hydraulic conductivity (K) were determined using the Theis-type curve match point method for confined aquifers (Fetter, 2001):

$$T = \frac{Q}{4\pi(h_o - h)} W(u) \text{ AND } K = \frac{T}{b} \quad (2)$$

Where: Q = pumping rate (ft³/d units)

$(h_o - h)$ = the drawdown (ft units)

$W(u)$ = the well function of u

b = aquifer saturated thickness (ft units)

The physical values of well W-2 were determined to be: transmissivity $15.9 \text{ ft}^2/\text{d}$ and hydraulic conductivity 0.23 ft/d . The results of the aquifer pump test at this location are reasonable, given extremely slow flow through a confining layer.

Ground water monitoring well W-3 (Figure 4 above) is located ~1037 feet from the center of the test site square along the access road/former railroad bed. The water-bearing stratum is low permeability shale with minor limestone layers; this well will pump dry in ~30 minutes at a pumping rate of ~17 gpm. The physical values of well W-3 could not be determined; false readings were observed during four different testing events that rendered the data collected during each of these events inaccurate; this was probably associated with rock fractures.

To ensure good controls of the natural water chemistry of the local area, homeowners to the east and west (up and downstream) along Fish Creek were approached with a short description of our intentions, and a question of permission to sample their domestic ground water supplies was posed if the criteria were met. The criteria for inclusion as a control were: naturally derived water with at least some residence time underground, i.e. well or spring-fed supplies with no filtration or other water treatment system. A total of six locations were selected, five ground water wells of varying depths and one spring-fed supply. The selected homeowners, after giving permission to sample their water supply, were then asked a series of questions regarding the construction of the supply being sampled. Table 2 outlines the known specifications of the domestic water supplies used for this study.

Sampling point	Owner	Location (WV)	Supply	Type	Depth (ft)	Uses	Pump
G-1	Joe Gorby	Georgetown	Well	Drilled	55	All	Electric
G-2	Amanda Gorby	Georgetown	Spring-fed	Free-flowing	Not applicable	All	None
G-3	Joe Gorby	Georgetown	Well	Hand-dug	20	Drinking	Manual
G-4	Marvin Mackey	Georgetown	Well	Drilled	40*	All	Electric
B-1	Mary Mackey	Bellton	Well	Drilled	34	All	Electric
B-2	Kathleen Mackey	Bellton	Well	Drilled	60	All	Electric

Table 2: Known specifications of domestic supply water sources; these sources are used as controls for the general water chemistry of the area around the research site.

**impeded by sediment at specified depth; true well depth is rumored to be ~180 ft.*

Ground and surface water data were collected from the test site and surrounding area beginning in October 2008 and ending in late 2013. The actual test site was sampled weekly while the surrounding area was sampled on a biweekly basis until calendar year 2011 when the routine was changed to a monthly basis; the Bellton (B-series) wells were dropped from the study in May 2010 at the homeowners' request.

The typical research site ground water extraction and collection method was as follows: The first measurement taken was depth from casing top to the water table (DTW) using either a Heron or EnviroTech electric well line in 0.10 feet increments. After the DTW was measured, the well was pumped for equipment rinsing, field measurements, and water sample preparation/collection. Once the pump was engaged the water was allowed to flow undisturbed for ~1 minute to eliminate any stagnant water within the well liner and screen. Once the well was cleared, the equipment used for water sample field analyses, preparation, and collection had been rinsed a minimum of three times before the water sampling process began.

The first step was to record temperature ($^{\circ}\text{C}$), pH in standard units (S.U.), and electrical conductivity (EC) ($\mu\text{S}/\text{cm}$) using a Fisher Scientific Accumet multi-parameter meter, model AP71 and/or AP85, and the associated probe(s). The probe(s) were rinsed two times before being placed into the final water sample, once with deionized water and once with sample water. The sample for analysis was recorded within one minute of water extraction. Another field test performed was for total sulfide ($\text{H}_2\text{S}_{(\text{aq})}$, $\text{HS}^{1-}_{(\text{aq})}$, $\text{S}^{2-}_{(\text{aq})}$) concentration using a Hach® Company Sulfide Test Kit, which is a color comparator method using 0.02 molar sulfuric acid ($\text{H}_2\text{SO}_{4(\text{aq})}$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})}$). Once all field observations and data had been collected and recorded, the preparation of water samples for transport and analysis began.

Three types of water samples were taken for two general analyses, total and dissolved ions. All water sample collection bottles were rinsed three times before final collection, which included one each of the following: a 500 mL bottle of raw water (for pH and anion analysis); a 125 mL bottle of raw water with 0.5 mL of 6 molar hydrochloric acid ($\text{HCl}_{(\text{aq})}$) added (for total cation analysis); and a 125 mL bottle of filtered ($0.45\mu\text{m}$ pore size) water with the 0.5 mL of $\text{HCl}_{(\text{aq})}$ added (for dissolved cation analysis). The water samples were then packed in ice for transport to the CONSOL Energy Inc. Research and Development Laboratory, located in South Park Pennsylvania, for analyses of total and dissolved major and minor cations: aluminum ($\text{Al}^{3+}_{(\text{aq})}$), calcium ($\text{Ca}^{2+}_{(\text{aq})}$), ferrous iron ($\text{Fe}^{2+}_{(\text{aq})}$), magnesium ($\text{Mg}^{2+}_{(\text{aq})}$), manganese ($\text{Mn}^{2+}_{(\text{aq})}$), potassium ($\text{K}^{1+}_{(\text{aq})}$), and sodium ($\text{Na}^{1+}_{(\text{aq})}$); and major anions: bicarbonate ($\text{HCO}_3^{1-}_{(\text{aq})}$), chloride ($\text{Cl}^{1-}_{(\text{aq})}$), nitrate ($\text{NO}_3^{1-}_{(\text{aq})}$), and sulfate ($\text{SO}_4^{2-}_{(\text{aq})}$). Another major anion within the local system, bisulfide ($\text{HS}^{1-}_{(\text{aq})}$), was field tested for (see above). Domestic water supply sample collection procedures were identical to research site ground water sampling procedures except for the depth to the water table, which was not measured for the domestic water supply wells. Surface and

spring water samples collected for field and laboratory analyses follow the same procedures as ground water samples, except that the total sulfide analysis was not utilized for waters in direct contact with the atmosphere.

Stream discharge data were collected when conditions permitted. These data were obtained using a Marsh-McBirney flow meter attached to a wading rod for depth measurements. The depth (in ft units), flow velocity (in ft/s units), and total width (in ft units) for stream subsections were taken both across and back the width of the stream at each specific sampling point. The total width was divided into one foot subsections; it was at these subsections where flow velocity measurements were taken, with the flow sensor set at 0.4 of the height of the stream above streambed bottom. The discharge volume was calculated using the following equation (Fetter, 2001):

$$Q = \sum(A_i * V_i) \quad (3)$$

Where: Q = discharge (ft³/s)

A_i = depth (ft) * width of stream subsection (ft)

V_i = velocity at stream subsection (ft/s)

i = 1 to n , where n = number of subsections of stream

Upon receiving the quantified chemical analytical data results from the laboratory, the data were quantified further via the computer software program Visual MINTEQ (VM), for percent charge balance error, and visual analysis, with outliers in the data set(s) being investigated; if outliers in the data existed, the first step was to rule out human and/or analytical error. The percent charge balance error is based on total equivalent concentration of dissolved

cations versus total equivalent concentration of total anions, which was calculated via VM, where:

$$\frac{[\Sigma \text{ cations } (\frac{eq}{L}) - \Sigma \text{ anions } (\frac{eq}{L})]}{[\Sigma \text{ cations } (\frac{eq}{L}) + \Sigma \text{ anions } (\frac{eq}{L})]} \times 100\% \quad (4)$$

Acceptable standard percent thresholds for charge balance error for this project were less than 5% for ground water, and less than 7% for stream and spring waters. Once the ion values causing the imbalance were determined, two different avenues were followed to fix the erroneous data. If the data causing the imbalance were cations, the total cation value was typically used in lieu of the dissolved cation data. If the total cation value did not fix the percent charge balance error or if the erroneous data were anion(s), the data in question were corrected via scatter graph plots, where field EC was plotted on the abscissa axis and compared to the equivalence of the ion in question on the ordinate axis. Once it was determined where the error existed, the corrected concentration value was determined via extrapolation horizontally from the measured field EC value to the ordinate axis and the associated equivalence value at the intersection; the new value was ultimately converted to mg/L units and substituted into VM where a new percent charge balance error was calculated.

Once the percent charge balance was within the acceptable thresholds set, the data were analyzed for the environmental effects of CCS/ECBM recovery. The dissolved carbon dioxide concentrations (d-CO₂ or CO_{2(aq)}) of the associated waters were determined using the following equation (Langmuir, 1997):

$$PCO_2(\text{bars}) * K_{CO_2} = CO_2 M \quad (5)$$

Equation 3 represents the chemical reaction:

Where: PCO_2 was derived from VM using field pH values.

K_HCO_2 was the tabulated Henry's Law constant in $M/bars$ units (Langmuir 1997).

The K_HCO_2 values were calculated based on a tabulated temperature range (corresponding to actual water sample temperature) and the following equations, based on Langmuir (1997):

$$\log_{10}K_HCO_2 = -0.0138 * (T - 10) + -1.273 \quad (7)$$

$$K_HCO_2 = 10^{\log_{10}K_HCO_2} \quad (8)$$

Where:

-0.0138 is the trend of the line slope of the negative difference for $\log_{10}K_HCO_2$ values at 10°C and 15°C , divided by the difference in temperature range ($15^\circ\text{C} - 10^\circ\text{C}$).

T is the actual water sample temperature.

-1.273 is the $\log_{10}K_HCO_2$ at 10°C .

Equation 5 above represents the formula used for water sample temperatures with a range between 10°C and 15°C , which was the most common temperature range observed within the ground water samples.

Head space gases: Shallow soil zone gas monitoring began with the construction of five, ~ 5 to 6 feet deep, monitoring wells, specific for the task, in May 2011, with well replacement, modification, and additional well construction occurring as needed. At the conclusion of the test site study, there were a total of 11 shallow soil zone monitoring wells; seven online and four offline due to the continued infiltration of water and/or difficulty of access. Figure 4 above

shows the locations of the shallow soil zone gas monitoring wells and the valley floor CBM production wells, MH-11 and MH-12, which were located at the southeast corner of the test site.

The shallow soil zone gas monitoring wells were constructed with two inch I.D. schedule 40 PVC casing and 20 slot screen, a pointed bottom end cap, and a two inch compression top cap; figure 6 shows a cross section and the dimensions of a typical shallow soil zone monitoring well at the test site. Each soil zone monitoring well bore was constructed using a 3 inch stainless steel hand auger to a target depth of between five and six feet or refusal, whichever came first. Each screened section was cut to a length of 2.5 feet and fitted with a 0.5 feet bottom pointed end cap. The upper casing was attached to the screened length via preexisting threads or the appropriate coupling, depending on the cut material. The void portion of the annulus zone was filled with coarse grain sand to ~2.5 inches above the screened length top with 0.5 inch bentonite clay pellets above the sand to ~3 inches above the surface. Weekly soil gas data were collected beginning approximately one week after well installation as to let the disturbed soil gas settle to undisturbed concentration levels. The cap design, construction, implementation, and modifications to accommodate isotope data collection were done by Brad D. Hega.

Figure 6: A typical test site shallow soil zone monitoring well, general soil composition of the area and soil depth range.

The $\text{CO}_{2(g)}$ and $\text{CH}_{4(g)}$ concentrations in each of the shallow soil zone gas monitoring wells were measured on a weekly basis. The measurements were taken directly in the field from the wells using a modified airtight septum to ensure absolute minimum atmospheric gas exchange during data collection. The instruments used to obtain the gas data are a Vaisala Industries MI-70 handheld indicator (meter and probe) for $\text{CO}_{2(g)}$ data collection, and an iBRID MX6 multi-gas monitor (monitor) for $\text{CH}_{4(g)}$ data collection. All pertinent ambient conditions (atmospheric pressure and head space temperature) for accurate $\text{CO}_{2(g)}$ measurements were

obtained and entered into the Vaisala meter. The detection probe of the Vaisala meter was suspended in-situ within the screened interval of the soil gas monitoring wells and was left to stabilize ~2-5 minutes before data were recorded.

Perfluorocarbon tracers: Two types of perfluorocarbon (PFC) tracers were injected by Arthur Wells and J. Rodney Diehl of the United States Department of Energy (USDOE) National Energy Technology Lab (NETL), simultaneously along with CONSOL Energy Inc. injection of CO_{2(g)} into each of two CO_{2(g)} injection wells: MH-18 and MH-20. The PFC tracer injection took place over a seven day period, April 15-22, 2011, with 500 mL of perfluorotrimethylcyclohexane (PTCH) tracer injected into CO_{2(g)} injection well MH-18, and 500 mL perfluoromethylcyclohexane (PMCH) tracer injected into CO_{2(g)} injection well MH-20. The head space gas of two CH_{4(g)} production wells, MH-11 and MH-12 (Figure 3 above) was sampled for weekly by passing 3 liters of head space gas through CATS sorbent tubes for laboratory analysis of PFC tracer adsorption.

Discussion and Results

Domestic Water Supplies: Tables 3 through 5 below show the average value of select parameters regarding the water chemistry of the eastern and western domestic supply control wells and spring.

Domestic Water Supply Location	From (date)	To (date)	Average Field pH (std units)	Average Field EC ($\mu\text{S}/\text{cm}$)	Average H_2S (mg/L)	Average $\text{PCO}_{2(\text{aq})}$ (atm)	Average Saturation index of calcite (based on Field pH)
G-1	Oct-08	Apr-12	8.56	467	0.07	9.08E-04	0.277
G-2	Oct-08	Apr-12	6.85	257	NA	1.95E-02	-1.250
G-3	Oct-08	Apr-12	5.62	238	ND	5.32E-02	-3.410
G-4	Oct-08	Apr-12	7.83	591	0.73	2.99E-03	-0.121
B-1	Oct-08	May-10	7.09	788	0.03	2.16E-02	-0.296
B-2	Oct-08	May-10	7.24	794	0.03	2.05E-02	-0.043

Table 3: Average values for select domestic supply water parameters across the study.

Domestic Water Supply Location	From (date)	To (date)	Average Ca^{2+} (mg/L)	Average Mg^{2+} (mg/L)	Average Na^{1+} (mg/L)	Average K^{1+} (mg/L)
G-1	Oct-08	Apr-12	8.5	1.5	103	1.0
G-2	Oct-08	Apr-12	32.4	6.2	8	1.4
G-3	Oct-08	Apr-12	16.0	4.3	10	12.7
G-4	Oct-08	Apr-12	23.5	3.3	97	1.7
B-1	Oct-08	May-10	73.5	13.2	67	2.0
B-2	Oct-08	May-10	61.7	8.6	99	2.2

Table 4: Average values for dissolved cations in domestic supply water across the study.

Domestic Water Supply Location	From (date)	To (date)	Average HCO_3^{1-} (mg/L)	Average Cl^{1-} (mg/L)	Average SO_4^{2-} (mg/L)	Average HS^{1-} (mg/L)	Average NO_3^{1-} (mg/L) as Nitrogen
G-1	Oct-08	Apr-12	279	6	1.8	1.35	ND
G-2	Oct-08	Apr-12	104	10	22.7	NA	1.2
G-3	Oct-08	Apr-12	22	18	32.2	ND	27.2
G-4	Oct-08	Apr-12	197	75	5.2	2.83	ND
B-1	Oct-08	May-10	263	104	21.1	0.03	ND
B-2	Oct-08	May-10	365	73	1.3	0.03	ND

Table 5: Average values for total anions in domestic supply water across the study.

*ND – None detected; *NA – Non-applicable

The natural ground water chemistry of the region varies with depth and location. The eastern G-type wells vary from basic (pH > 7.00 S.U.) to acidic (pH < 7.00 S.U.). The well with the highest pH is well G-1 at a drilled depth of ~55 feet. The distinct features of the chemistry of well G-1 are: the elevated dissolved monovalent cation concentrations, the depleted dissolved divalent cation concentrations, the elevated concentrations of $\text{HCO}_3^{1-}(\text{aq})$ and $\text{HS}^{1-}(\text{aq})$, and the depleted concentration of $\text{SO}_4^{2-}(\text{aq})$. The elevated and depleted ion concentrations appear to be the products of both the shale rich subsurface environment and the intrusion of naturally occurring $\text{CH}_{4(\text{g})}$ into the fresh ground water zone. The ground water associated with well G-1 also has a strong $\text{H}_2\text{S}_{(\text{g})}$ odor and according to residents and the now defunct Springhill Well Services, $\text{H}_2\text{S}_{(\text{g})}$ is first detected via olfactory sense at a depth of ~50 feet and gets progressively worse with increased depth. The following chemical reaction could be contributing to the $\text{H}_2\text{S}_{(\text{g})}$ in the system:

Chemical equation 9 could also explain the oversaturation of calcite (high SI_c) observed at this particular ground water sampling location (Table 3 above), due to elevated bicarbonate and hydroxyl ion concentrations (high pH).

Wells G-3 and G-4 are not indicative of the regional ground water. Well G-3 is an uncased, hand-dug well ~20 feet deep with a hand pump atop a brick structure for water extraction. The most distinct features of the chemistry in well G-3 are the acidic pH (< 7.00 S.U.), the abnormally high potassium ($\text{K}^{1+}(\text{aq})$) concentration relative to sodium ($\text{Na}^{1+}(\text{aq})$) ($\text{K}^{1+} > \text{Na}^{1+}$), and the high (> 10.0 mg/L) dissolved nitrate ($\text{NO}_3^{1-}(\text{aq})$) nitrogen concentration. The acidic pH is due to the influence of rain water, a short ground residence time, and shallow depth. The

high $K^{1+}_{(aq)}$ and $NO_3^{1-}_{(aq)}$ concentrations are a result of nonpoint source pollution via agricultural activities (livestock waste and fertilizers) and septic leachate in the form of potassium nitrate ($KNO_{3(aq)}$) from the higher terrain to the NNW; this well has caused two suspected cases of Blue Baby Syndrome.

Well G-4 is speculated to be ~180 feet below the surface, although when a total depth measurement was attempted, the probe became impeded by sediment starting at a depth of 38 feet, but was able to proceed to a depth of 40 feet until becoming trapped within the sediment. Well G-4 is constructed in a manner that allows for surface runoff to enter the well bore and for soil/rock collapse within the said bore; the well is flush with the ground surface, has an open top cap, and is only cased to 1.7 feet below the ground surface. The pump unit for extraction is near the bottom of the well bore within the sediment column. Due to the various densities of different sized particles, the larger, heftier particles will likely reside near the bottom of the well bore, which is the reason sediment has not impeded the production of well G-4. Due to the factors described above, the chemistry of the ground water extracted from well G-4 is highly unreliable. For instance, it is impossible to determine the source of the high $Na^{1+}_{(aq)}$ $Cl^{1-}_{(aq)}$ concentrations as it could be subsurface generated (alleged depth) or from surface activities. It is interesting to note the extremely high $HS^{1-}_{(aq)}$ and $H_2S_{(g)}$ concentrations associated with well G-4, which are probably due to location and alleged extreme depth. One aspect of well G-4 can confidently be stated; sulfur reducing bacteria are probable there given a black slimy substance forming on the sides of the toilet bowls and tanks and the extremely high concentrations of $HS^{1-}_{(aq)}$ and $H_2S_{(g)}$, that may indicate sulfate ($SO_4^{2-}_{(aq)}$) reduction caused by methane gas. Of the two drilled G-type wells, G-1 is the best representation of the regional ground water to the east of the test site.

The western B-type wells are slightly basic ($\text{pH} > 7.00$ S.U.), with average $\text{HCO}_3^{1-}(\text{aq})$ concentrations exceeding 250 mg/L in each of the two wells. The overall chemistry of the B-type wells indicates the aquifer(s) which these particular wells are penetrating may be slightly contaminated with salt water either naturally or via anthropogenic enhanced origins. The chemistry of the domestic supply ground water wells in the Bellton, WV area may not be a good representation of the regional ground water to the west of the test site.

The water associated with domestic supply G-2 is a spring type supply that receives recharge on/near the hilltops south of Fish Creek; G-2 water resurfaces above the valley bottom so it therefore has little consequence to the deeper aquifers associated with this research. The pH of the spring supply is slightly acidic ($\text{pH} < 7.00$ S.U.) and is one of two sampling locations to test positive for $\text{NO}_3^{1-}(\text{aq})$, albeit at low concentrations (< 5.0 mg/L). The detectable $\text{NO}_3^{1-}(\text{aq})$ is due to natural sources as the source area above the source spring is undeveloped.

The overall chemical analytical analysis of the data associated with both eastern (Georgetown) and western (Bellton) domestic water supplies show no apparent chemical effects from test site activities from $\text{CO}_{2(\text{g})}$ sequestration and $\text{CH}_{4(\text{g})}$ recovery.

Test Site Waters: The data reviewed here will cover the entire study period, beginning October 2008 through mid-2014. Although the chemical properties of the surface waters will be discussed, they are of lesser importance due to the lower residence time of any potentially escaping $\text{CO}_{2(\text{g})}$ within the stream. The shallow ground water monitoring wells within the test site square are the most important aspect of the water study from a hydrogeologic standpoint as the ground water could be encountered to a great extent by any potentially escaping $\text{CO}_{2(\text{g})}$ and also due to residence time of the $\text{CO}_{2(\text{g})}$ should it migrate into the fresh ground water zone.

During the study period, no significant trends in the calculated dissolved $\text{CO}_{2(\text{aq})}$ data have been observed, for either ground water or stream water.

Test Site Surface Water: The stream bisecting the site, as mentioned earlier, is the Pennsylvania Fork of Fish Creek where three stream water sampling locations were selected at strategic locations S-1, S-2, and S-3, which are east, center, and west respectively relative to the test square. See Figure 4 above for their locations. Tables 6 through 8 below show the average value of select chemical parameters at stream water sampling locations S-1, S-2, and S-3. Water sampling at location S-3 had to be discontinued in January 2011 as the only safe access route to it was eroded away via flood waters. The remaining stream water sampling locations, S-1 and S-2 were discontinued in June of 2013 as the test site study was beginning to conclude, so that remaining funds could be used to continue ground water sample collection and processing as long as possible.

Stream Location	From (date)	To (date)	Average Field pH (std units)	Average Field EC ($\mu\text{S}/\text{cm}$)	Average $\text{PCO}_{2(\text{aq})}$ (atm)	Average Saturation index (calcite) based on Field pH
S-1	Oct-08	Jun-13	7.66	205	3.31E-03	-0.639
S-2	Oct-08	Jun-13	7.78	225	2.07E-03	-0.530
S-3	Oct-08	Jan-11	7.75	272	2.96E-03	-0.497

Table 6: Average values for select stream water parameters across the study period.

Stream Location	From (date)	To (date)	Average Ca^{2+} (mg/L)	Average Mg^{2+} (mg/L)	Average Na^{1+} (mg/L)	Average K^{1+} (mg/L)
S-1	Oct-08	Jun-13	25.5	4.28	6.85	1.93
S-2	Oct-08	Jun-13	25.6	4.34	8.75	1.88
S-3	Oct-08	Jan-11	29.0	5.00	15.1	2.12

Table 7: Average values for dissolved cations in stream water across the study period.

Stream Location	From (date)	To (date)	Average HCO_3^{1-} (mg/L)	Average Cl^{1-} (mg/L)	Average SO_4^{2-} (mg/L)	Average NO_3^{1-} (mg/L) as N
S-1	Oct-08	Jun-13	82	8	19.2	0.641
S-2	Oct-08	Jun-13	81	13	19.2	0.629
S-3	Oct-08	Jan-11	86	27	19.2	0.751

Table 8: Average values for total anions in stream water across the study period.

*ND – None detected; *NA – Non-applicable

Figures 7 – 15 show the average monthly data for specific chemical parameters at each of the three stream water sampling locations. Each data point on the graph plots is the average of generally between three and five weekly stream water samples.

Figure 7: Average monthly stream discharge through time. The highest discharge values occur during the wet (winter through spring) seasons.

Figure 8: Average monthly test site stream water field measured pH through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 9: Average monthly test site stream water field measured electrical conductivity through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 10: Average monthly test site stream water dissolved $\text{CO}_{2(\text{aq})}$ concentrations based on chemical equilibria, $\text{PCO}_{2(\text{aq})}$, and field pH through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.

Figure 11: Average monthly test site stream water dissolved cation concentrations at sampling point S-1 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 12: Average monthly test site stream water total anion concentrations at sampling point S-1 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.

Figure 13: Average monthly test site stream water dissolved cation concentrations at sampling point S-2 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 14: Average monthly test site stream water total anion concentrations at sampling point S-2 through time. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.

Figure 15: Average monthly test site stream water dissolved cation concentrations at sampling point S-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 16: Average monthly test site stream water total anion concentrations at sampling point S-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

The overall chemistry of the stream has stayed fairly consistent among sampling locations throughout the study period with the lone exception to the consistency occurring at sampling locations S-2 and S-3 at the beginning of sample collection in October 2008 through the first high flow event in early December 2008.

Figures 11 and 12 above show the major cation and anion at stream location S-1 to consistently be $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{HCO}_3^{1-}_{(\text{aq})}$ respectively. All cation and anion concentrations at this particular sampling location have stayed within acceptable limits; no elevated concentrations or pollution events were detected.

Figures 13 and 14 above show the major cation and anion at stream location S-2 to consistently be $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{HCO}_3^{1-}_{(\text{aq})}$ respectively; however, there is an exception in late 2008 when $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ were the dominant or nearly dominant ions.

Figures 15 and 16 above show the major cation and anion at stream location S-3 to consistently be $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{HCO}_3^{1-}_{(\text{aq})}$ respectively; however, there is an exception in late 2008 when $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ were the dominant ions and in higher concentrations than observed at location S-2.

The fluctuations of the major ions $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{HCO}_3^{1-}_{(\text{aq})}$ at each of the stream water sampling location represents a dilution effect due to seasonality with the lower concentrations occurring during the winter and spring when water levels were generally higher due to increased precipitation and snowmelt causing increased stream discharge than during the wet (winter through spring) seasons (Figure 7).

The abnormally high $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ concentrations observed along with a comparison of EC at the three stream locations (Figure 9 above) for late 2008 indicate a source of brine pollution then, located between stream locations S-1 and S-2.

Figure 17 represents the layout of what would become the center of the test site and the conditions on July 26, 2007. During a surveying trip to the future test site on July 26 2007, one of the investigators observed the mainline valve of a series of 4 residual brine water holding tanks open one quarter turn, allowing the residual brine (coal bed formation) water to leak onto and into the surrounding soil; the investigator closed the valve and reported the finding. It is important to note, the test site functioned as a coal bed methane production site for ~3 years prior to any $\text{CO}_{2(\text{g})}$ injection related activities occurring.

Figure 17: Map view of the area on July 26, 2007; this became the center of the test site square and where the CO_{2(g)} injection system is located via UTM meter grid values.

During the production of CBM from the wet Pittsburgh and Upper Freeport coal seams, formation water was produced along with the gases; the formation water was separated from the gas and stored until hauled away via special waste hauling trucks for processing at the appropriate facility. The waste water service that was contracted to remove the residual brine formation water from the test site from ~2006 to ~2010 was charged by the Pennsylvania Attorney General's Office with 175 criminal counts, some of which included the illegal dumping of waste water into abandoned mine shafts and streams in a six county region throughout southwestern Pennsylvania.

The following is evidence for brine water pollution having occurred in Fish Creek during late 2008: Criminal charges against waste water service contractor; the contractor's affiliation with CNX gas at the time; the rural location of the future test site; the high EC levels at stream water sampling locations S-2 and S-3; the high $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ concentration values at locations S-2 and S-3; the position of the brine tank discharge valve (open one quarter turn); and the fact these high stream chemical values returned to normal levels after the next significant high water event never to return (possibly due to our presence at the test site). The evidence, albeit circumstantial, suggests, unbeknownst to CNX gas and CONSOL Energy Inc., that the waste water service contractor was involved in the illegal, on site dumping of residual brine waste water at the Georgetown CBM production site.

Test Site Ground Water: Tables 9 through 11 below show the average value of select parameters regarding the test site ground water chemistry of the three ground water monitoring wells within the test site square.

Water Well Location	From (date)	To (date)	Average Field pH (std units)	Average Field EC ($\mu\text{S}/\text{cm}$)	Average H_2S (mg/L)	Average $\text{PCO}_{2(\text{aq})}$ (atm)	Average Saturation index (calcite)
W-1	Oct-08	Oct-13	8.39	1105	0.037	1.16E-03	0.621
W-2	Oct-08	Oct-13	8.70	634	0.017	3.37E-04	0.148
W-3	Oct-08	Oct-13	9.28	829	0.005	1.84E-04	-0.017

Table 9: Average values for select test site ground water parameters across the study period.

Water Well Location	From (date)	To (date)	Average Ca^{2+} (mg/L)	Average Mg^{2+} (mg/L)	Average Na^{1+} (mg/L)	Average K^{1+} (mg/L)
W-1	Oct-08	Oct-13	34.6	5.07	171	1.19
W-2	Oct-08	Oct-13	7.49	1.27	127	1.00
W-3	Oct-08	Oct-13	0.88	0.22	199	0.69

Table 10: Average values for dissolved cations in test site ground water across the study period.

Water Well Location	From (date)	To (date)	Average HCO_3^{1-} (mg/L)	Average Cl^{1-} (mg/L)	Average SO_4^{2-} (mg/L)	Average HS^{1-} (mg/L)	Average NO_3^{1-} (mg/L)
W-1	Oct-08	Oct-13	298	157	5.59	0.531	0.114
W-2	Oct-08	Oct-13	184	95	7.93	0.473	ND
W-3	Oct-08	Oct-13	449	31	3.77	0.587	0.141

Table 11: Average values for total anions in test site ground water across the study period.

*ND – None detected; *NA – Non-applicable

Figures 18 – 20 show the average monthly data for field measured pH, electrical conductivity (EC), and calculated $\text{CO}_{2(\text{aq})}$ at ground water well sampling locations W-1, W-2, and W-3, while Table 12 compares the average EC values of ground water well W-2 to various stages of $\text{CO}_{2(\text{g})}$ injection activities. Figures 21 and 22 below highlight the major cation and major anion concentrations observed in the ground water from ground water sampling well W-1. Each data point on the graph plots is the average of generally between three and five weekly ground water samples.

Figure 18: Average monthly test site ground water field measured pH through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 19: Average monthly test site ground water field measured electrical conductivity through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

CO_{2(g)} Injection Period Phase	Monthly Average Field EC ($\mu\text{S}/\text{cm}$)	Field EC; difference from background	Field EC; % increase above background
Background until September 7, 2009	574	0	0
Manual Sept. 2009 to Dec. 2009 March 2012 to July 2012	629	55	9.6
Automated Jan. 2010 to June 2011 Aug. 2011 to Oct. 2011 Aug. 2012 to Jan. 2013 July 2013 to Oct. 2013	650	76	13.2
Lull July 2011 Nov. 2011 to Feb. 2012 Feb. 2013 to June 2013	635	61	10.6

Table 12: The differences among average electrical conductivity values from background of the ground water from test site well W-2 during different phases of CO_{2(g)} injection activity; note the period during automated injection has the highest positive difference.

Figure 20: Average monthly dissolved CO_{2(aq)} concentrations through time, based on test site ground water chemical concentrations, chemical equilibria, PCO_{2(aq)}, and field pH through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 21: Average monthly dissolved cation concentrations for test site ground water at well sampling well W-1 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 22: Average monthly test site ground water total anion concentrations at well sampling point W-1 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

The chemistry of the ground water at the test site varies to an extent among the three ground water monitoring wells due to variable depth of the static water table, aquifer strata, or pollution. The pH is high (pH > 7.00 S.U.) for all three ground water monitoring wells with the highest pH values occurring in well W-3, which has a monthly average field pH value of ~9.30 S.U. (Figure 18). Tables 9, 10, and 11 above highlight the average chemistry of the test site ground water across the study period.

Figure 21 and Figure 22 above show the major cations and major anions present in well W-1; $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ are present in elevated concentrations. The $\text{HCO}_3^{1-}_{(\text{aq})}$ concentration is also elevated, but the elevated levels are due, in most part, to the natural chemical weathering in the subsurface environment.

Possible explanations for the elevated $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}^{1-}_{(\text{aq})}$ include: an upwelling of deep seated formation water; the proximity of well W-1 to $\text{CH}_{4(\text{g})}$ production wells MH-11 and MH-12 (~170 feet) (Figure 4 above); the natural and/or anthropogenic induced intrusion of $\text{CH}_{4(\text{g})}$ into the freshwater aquifer; a slop tank spill near the present holding tanks adjacent to the $\text{CH}_{4(\text{g})}$ production wells (~300 feet from well W-1) in August 2006; or some combination thereof. The area of the spill was remediated and sampled (minus nuisance contaminants) by Weavertown Environmental Group (WEG) on August 23 and 24, 2006.

The slop tank spill is the least likely source of the elevated values for a variety of reasons. The length of time elapsed between the spill and ground water monitoring (~2.5 years); the high transmissivity and hydraulic conductivity of the aquifer (see well physical properties above); and the fact the soil was removed from the site makes it an unlikely scenario that the slop tank contents are still affecting the area.

Although $\text{CH}_{4(\text{g})}$ has been detected sporadically in the head space of well W-1, it was never measured to be above 2% by volume on any given day. Table 13 below shows a comparison of the average head space methane values in wells W-1, W-2, and W-3 from March 2011 through March 2014; wells W-1 and W-2 contain 0.8% and 0.1% respectively of the methane concentrated within the head space of well W-3 on average. Considering the data and the lack of the geochemical signatures of significant $\text{CH}_{4(\text{aq})}$ contamination, it is unlikely CH_4 in any phase state is having an effect on the aquifer for well W-1.

Water Well Location	From (date)	To (date)	Average Head Space CH _{4(g)} (volume %)
W-1	Mar. 2011	Mar. 2014	0.121
W-2	Mar. 2011	Mar. 2014	0.020
W-3	Mar. 2011	Mar. 2014	14.3

Table 13: Average CH_{4(g)} volume percent concentration in the head space of each test site shallow ground water monitoring well across the CH_{4(g)} data collection period.

The source of the elevated ions in the ground water within the aquifer at well W-1 was more than likely the nearly continuously operating pump jack associated with PCB CH_{4(g)} production well MH-12. The pump jack may have been contributing to the elevated ion levels in a number of ways. On numerous occasions throughout the study, formation water was observed discharging from the top of the production string during upstroke of the pump jack; these events occurred so often, the ground around this area was stained orange (Figure 23), but has since been covered with new limestone gravel. Figure 23 below shows the labeled areas of interest around the pump jack associated with CH_{4(g)} production from well MH-12.

Figure 23: Potential point source of brine pollution from coal bed formation water. Brine water has been observed emanating from the area of the MH-12 CH_{4(g)} production well pump jack, where the polished rod enters the casing head; note the wet, iron stained ground, which has since been covered with fresh limestone gravel (Figure photo taken 3/20/2009).

The failing of the seal for the polished rod within the casing and the possibility of casing and/or borehole failure, especially the former, makes this particular pump jack the likely source of the elevated EC and ion levels of Na¹⁺_(aq) and Cl¹⁺_(aq) in the aquifer well W-1 penetrates.

Figures 24 and 25 below highlight the major cation and major anion concentrations observed in the ground water from ground water sampling well W-2. Each data point on the graph plots is the average of generally between three and five weekly ground water samples.

Figure 24: Average monthly test site ground water dissolved cation concentrations at ground water well sampling point W-2 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 25: Average monthly test site ground water total anion concentrations at ground water well sampling point W-2 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 24 and Figure 25 above show the major cation and major anions present in well W-2, Na¹⁺_(aq), Cl¹⁻_(aq), and HCO₃¹⁻_(aq), are present in elevated concentrations, but to a lesser extent than these concentrations at well W-1. Possible explanations for the elevated Na¹⁺_(aq) and Cl¹⁻_(aq) include: an upwelling of deep seated formation water; the pollution event via the formation water holding tanks discussed with surface water illustrated in Figure 16 above; or the intrusion of CH_{4(g)} into the freshwater aquifer. Although the area around well W-2 often smelled of methanethiol (methyl mercaptan), no methane values greater than 0% were measured during

these odoriferous events and the data obtained from the ground water at W-2 show no geochemical signatures of CH₄ pollution.

The EC of the water in the aquifer at well W-2 (Figure 19 above) shows a slight upward trend during the course of the study; this trend may be a result of slight microseepage of injected CO_{2(g)} into the freshwater aquifer, with the following synthesis reaction occurring:

The deprotonation would cause chemical weathering of the surrounding strata, raising the concentration of cations and anions, which in turn would raise the EC of the ground water.

The most significant rise in EC for ground water well W-2 occurred during the longest sustained period of automated CO_{2(g)} injection from January 2010 to late June 2011, when CO_{2(g)} injection was nearly continuous. The close proximity of the injection system to well W-2 makes it the most likely sampling point to be impacted first by injected CO_{2(g)}. Considering the eastern dip trend of the subsurface strata, the podded and wet nature of the UFCB on the western side of the test site, and the location of well W-2 (east of MH-18, but slightly west of MH-20), injection well MH-18 is more likely to be impacting well W-2 than MH-20.

Figure 26 below correlates the injection borehole pressure of MH-18 to the field EC measured in the water from the aquifer at well W-2 via regression analysis using a 29 month lag time for prior CO_{2(g)} injection pressure. The lag time refers to the time elapsed since injection until the data showed a significant trend within a specified range of time. The correlation coefficients (R-values) must be significant at 0.01 α in order for the data to have any merit. The R value generated from the regression in Figure 26 is significant at 0.01 α ; the R² value shows 46.7% of the data can be attributed to the regression trend based on a 29 month lag basis. The regression trend data indicate sequestered CO_{2(g)} may take around two years to migrate to the

shallow aquifer at ground water well W-2. Regression trend data were analyzed on an average monthly basis with a zero to 48 months lag time since CO_{2(g)} sequestration began; the 29 months lag time data represents the strongest, most significant trend. However, the evidence represented by the regression trend data is purely circumstantial and does not prove the migration of injected CO_{2(g)} into the shallow aquifer.

Figure 26: Determination and correlation coefficients (R^2 and R respectively) of the down bore pressure of CO_{2(g)} injection well MH-18 versus the field measured electrical conductivity of the ground water from test site well W-2. The R value is significant at 0.01 α ; the R^2 value shows 46.7% of the data can be attributed to the regression trend based on a 29 months lag.

Figures 27 and 28 below highlight the major cation and major anion concentrations observed in the ground water from ground water sampling well W-3. Each data point on the graph plots is the average of generally between three and five weekly ground water samples.

Figure 27: Average monthly test site ground water dissolved cation concentrations at ground water well sampling point W-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

Figure 28: Average monthly test site ground water total anion concentrations at ground water well sampling point W-3 through time. The blue arrow indicates the pre CO₂ gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO₂ gas injection phase; the purple arrows indicate the nearly continuous (automated) CO₂ gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO₂ gas injection.

The major cation and major anion present respectively in well W-3 are Na¹⁺_(aq) and HCO₃¹⁻_(aq), which were present at elevated concentrations; Cl¹⁻_(aq) is also elevated, but to a much lesser extent than present in wells W-1 and W-2. Possible explanations for the elevated Na¹⁺_(aq) include: natural water softening in the subsurface environment (divalent/monovalent cation exchange on clay minerals in shale); well grout contamination due to the casing being seated in brittle fractured shale; or the intrusion and dissolution of CH_{4(g)} into the freshwater aquifer.

The extremely high pH and higher than normal concentrations of $\text{Na}^{1+}_{(\text{aq})}$, $\text{HCO}_3^{1-}_{(\text{aq})}$ and lower than normal concentrations of $\text{Ca}^{2+}_{(\text{aq})}$, $\text{Mg}^{2+}_{(\text{aq})}$, and $\text{SO}_4^{2-}_{(\text{aq})}$ at well W-3 (Tables 9, 10, and 11 above) suggest the intrusion and dissolution of $\text{CH}_{4(\text{g})}$ into the fresh water aquifer near well W-3. Table 13 above, based entirely on data collected by WVU personnel, shows a comparison of the average head space $\text{CH}_{4(\text{g})}$ percent volume concentrations of the three test site ground water monitoring wells throughout the $\text{CH}_{4(\text{g})}$ monitoring period. Figure 29 below graphically depicts the average monthly head space $\text{CH}_{4(\text{g})}$ percent volume concentration of well W-3 through time; this graph is based on a combination of all head space $\text{CH}_{4(\text{g})}$ data collected from well W-3 by WVU and CONSOL Energy Inc. personnel. The overall trend of Figure 29 is relatively flat through time; however, the method of data collection used by CONSOL Energy Inc. may have allowed for atmospheric mixing within the well head space, which would have diluted the $\text{CH}_{4(\text{g})}$ concentration, thus skewing the data. The ionic concentrations of well W-3 indicate $\text{CH}_{4(\text{aq})}$ has probably been present since ground water monitoring began, but it is important to note the ground water may have become conditionally saturated with $\text{CH}_{4(\text{aq})}$ after $\text{CO}_{2(\text{g})}$ injections activities commenced, allowing for higher concentrations of $\text{CH}_{4(\text{g})}$ to accumulate in the head space. If only data collected in 2011 and 2012 are considered, the overall trend is increasing through time, but to a lesser extent.

Figure 29: The volume percent concentration of $\text{CH}_{4(g)}$ in the head space of well W-3 through time. The data collected by CONSOL Energy Inc. personal are indicated by large black squares; the rest of the data were collected by WVU personnel. The blue arrow indicates the pre CO_2 gas injection phase (background); the black arrows indicate the daily, intermittent, manual CO_2 gas injection phase; the purple arrows indicate the nearly continuous (automated) CO_2 gas injection phase; and the red arrows indicate an extended shutdown (lull phase) of CO_2 gas injection.

According to Van Voast (2003), coal bed formation waters where CH_4 is present are effectively devoid of the divalent ions $\text{Ca}^{2+}_{(aq)}$, $\text{Mg}^{2+}_{(aq)}$, and $\text{SO}_4^{2-}_{(aq)}$ and contain primarily the monovalent ions $\text{Na}^{1+}_{(aq)}$ and $\text{HCO}_3^{1-}_{(aq)}$. Although uncommon in the hydrosphere, this type of chemical signature can occur in the absence of methane gas; however, a signature of this type is the first step to further $\text{CH}_{4(g)}$ exploration (Van Voast, 2003). A preliminary carbon isotope analysis conducted by Dr. Shikha Sharma at her West Virginia University laboratory indicates there is $\text{CH}_{4(aq)}$ present in the ground water and it does have a deep seated origin; the

stratigraphic log of the area indicates the nearest significant methane bearing formation to be the PCB at a depth of ~600 feet below the ground surface. Figure 30 below shows the chemical signatures of formation waters where $\text{CH}_{4(g)}$ is present and the chemical signatures where $\text{CH}_{4(g)}$ is absent. The waters associated with CBM are typified by the absence or extremely low concentration of the ions described above regardless of formation age or lithology (Van Voast, 2003).

Figure 30: Schoeller diagrams of the geochemical signatures typical of coal bed formation waters within CH_{4(g)} bearing coal seams. Graph f represents the geochemical signature of the ground water extracted from well W-3 (figure adapted from Van Voast, 2003).

A variety of chemical reactions take place when CH₄ is involved, which give these types of waters their unique geochemical signature. Microbial SO₄²⁻_(aq) reduction does occur in coal beds and may be occurring to an extent within the anoxic aquifer, but in the absence of significant organic matter, the shallow depth, and the likely surface seepage of CH_{4(g)} from depth, the following reduction and hydrolysis reactions are likely occurring within the shallow freshwater zone:

The reduction reaction (9) drives up the HCO₃¹⁻_(aq) concentration, which in turn causes a rise in pH to where the dominant S²⁻ species is HS¹⁻_(aq) (pH > 7.00 S.U.). The hydrolysis reaction (11) produces H₂S_(g) and OH¹⁻_(aq); the OH¹⁻_(aq) causes the pH to be driven higher (pH > 9.00 S.U.). The equivalence concentrations of SO₄²⁻_(aq) and HCO₃¹⁻_(aq) exhibit a significant, inverse correlation trend significant at 0.01 α with at least 46.5% of the HCO₃¹⁻_(aq) being generated via SO₄²⁻_(aq) reduction. Table 14 below shows the percent increase of the average in average monthly concentrations of the HCO₃¹⁻_(aq) in well W-3 when compared to the best ground water control well (G-1) and the other two test site wells (W-1 and W-2).

Well Location	W-3	W-1	W-2	G-1
HCO ₃ ¹⁻ _(aq) (mg/L)	456	288	184	278
% of W-3 (456)	100	65.1	40.6	61.0

Table 14: Average of the monthly average values of HCO₃¹⁻_(aq) concentrations in ground water wells and the percent of the HCO₃¹⁻_(aq) value observed in well W-3.

The depletion of the divalent cations Ca²⁺_(aq) and Mg²⁺_(aq) in a CH₄ rich environment is primarily caused by the inorganic precipitation of calcite (CaCO_{3(s)}) and to a lesser extent

dolomite ($\text{CaMg}(\text{CO}_3)_2(\text{s})$) due to reduced solubility in the presence of elevated $\text{HCO}_3^{1-}(\text{aq})$ concentrations (Van Voast, 2003).

Another geochemical process contributing to the depletion of $\text{Ca}^{2+}(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ is cation exchange with reactive clay minerals, whereby $\text{Ca}^{2+}(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ adsorb to the clay and are replaced in solution by equivalent concentrations of $\text{Na}^{1+}(\text{s})$ contained on the clay particles; the ratio is 1:2, 1 divalent cation (Ca^{2+}) for 2 monovalent cations (2Na^{1+}). Cation exchange of the type described above is natural water softening, which is more predominant in a shale dominant subsurface, which is the type of lithological environment at the test site.

The evolution of the chemical quality in well W-3 begins with dissolution of ions in recharge water; the reduction of $\text{SO}_4^{2-}(\text{aq})$ via $\text{CH}_4(\text{aq})$, which enriches $\text{HCO}_3^{1-}(\text{aq})$ and $\text{HS}^{1-}(\text{aq})$; and the hydrolysis of $\text{HS}^{1-}(\text{aq})$, which increases the $\text{OH}^{1-}(\text{aq})$ concentration, thus driving the pH > 9.00 S.U.. The depletion of $\text{Ca}^{2+}(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ occurs throughout the system by adsorption with clay minerals, and $\text{HCO}_3^{1-}(\text{aq})$ driven precipitation of calcite and dolomite (Van Voast, 2003). Figure 31 shows the average monthly $\text{HCO}_3^{1-}(\text{aq})$ concentration and calcite saturation index vs. calendar time for well W-3; these data have a nearly inverse relationship across the set, which is further indication of CH_4 pollution within the aquifer well W-3 penetrates.

Figure 31: Data plot for test site ground water monitoring well W-3 showing the monthly average values of $\text{HCO}_3^{1-}{}_{(aq)}$ concentration and ground water calcite saturation index through time.

Although the carbon present in well W-3 is from a deep seated origin, the source of the CH_4 contamination has not been determined. One possible $\text{CH}_{4(g)}$ source is a deep penetrating monitoring well located ~150 feet to the east of well W-3 along the access road. See Figures 32 and 33 below.

Figure 32: Location of deep monitoring bores MH-26 and MH-27 relative to shallow ground water monitoring well W-3 (adapted from Figure 4 above).

MH-26 and MH-27 are two deep penetrating (~1300 feet) monitoring wells located along the test site access road (Figure 32). The wells are designed to test the gases and water contained within the UFCB, the target formation for $\text{CO}_{2(g)}$ sequestration. It was determined via volumetric calculations the grout used in the annulus zone of MH-26 from ~310 feet to the surface was insufficient insofar as to assure a proper seal; however the area housing the insufficient grout is contained within the walls of two steel casings, i.e. a casing within a casing with grout in between.

Figure 33: Cross section of deep monitoring bore MH-26 in relation to ground water monitoring well W-3 and shallow vadose zone monitoring well W-3A moving from east (left side) to west (right side). The red interval at well W-3 is the open screened length of the borehole while the blue interval represents the cased length of the borehole. The blue line with upside down triangles represents the water table and red line with upside down triangles shows the approximate position of the fresh water/brine water interface.

The deep monitoring wells are constructed identically, with the only exception being the insufficient amount of grout in MH-26. The following descriptions are based on well MH-26. Figure 33 above is a schematic cross section of the underlying strata showing the penetration of well MH-26 through the UFCB. Deep monitoring well MH-26 was constructed as follows: a 4.5 inch diameter steel pipe extending from ~5 feet above the surface to ~75 feet below the UFCB serves as the well liner with a perforated section penetrating the width of the UFCB to allow coal seam water and/or gas to enter the well for extraction; the bore, housing the liner/perforated sections, is 6.25 inches in diameter, and is grouted to the surface. The liner is cased with a 9.6 inch diameter casing to a depth of 300 feet and is grouted to the surface. The casing is in turn

cased to 30 feet with a 13.6 inch diameter steel casing, which is not grouted, but filled with soil. The previously mentioned 6.25 inch diameter liner also has a 30 feet long section of fiberglass contained within the uncased length and coinciding with the PCB. The fiberglass section is coupled to the steel liner both above and below the contact with the PCB; this may also be an avenue for the intruding $\text{CH}_{4(g)}$.

There are at least two options for failure regarding the fiberglass section of liner. The first would be the tremendous weight of the overlying steel pipe attached to the fiberglass section which could cause (even subtle) fractures, which in turn could cause the grout outside of the fiberglass to displace. Secondly, a failure could occur at the steel/fiberglass contact due to the difference in materials being married and the previously mentioned weight of the overlying steel pipe. Once failure of the fiberglass and/or displacement of the grout occur, $\text{CH}_{4(g)}$ will channel through the annulus zone where the grout was displaced and begin to migrate laterally seeking the path(s) of least resistance to the surface. The ease of which $\text{CH}_{4(g)}$ will travel from the PCB is determined by the formation pressure, hydrostatic pressure, and hydrodynamic pressure; for simplicity, only formation pressure and theoretical hydrostatic pressure (the weight of the overlying water) is presented next.

The UFCB has a formation pressure of 455 pounds per square inch (psi) (Calderon, 2010) with a theoretical hydrostatic pressure of 524 psi (Harrison, May-June 1985), which yields a net downward pressure gradient of 69 psi. While the actual hydrostatic pressure would be lower due to hydrodynamic pressure, the pressure gradient of -69 is a reasonable assumption. It is important to note, the formation pressure of the UFCB may have changed (increased) drastically; this change of formation pressure would have started as soon as $\text{CO}_{2(g)}$ injection became steady.

The $\text{CH}_{4(g)}$ contained within the UFCB may or may not be contributing to the head space $\text{CH}_{4(g)}$ of well W-3.

The PCB, overlying the UFCB, has a formation pressure of 700 psi and a theoretical hydrostatic pressure of 223 psi (Bromhal, 2004), which creates an upward pressure gradient of 477 psi. Assuming some type of failure within the fiberglass length and the subsequent displacement of grout associated with MH-26, the PCB $\text{CH}_{4(g)}$ is likely the largest contributor to the pollution in well W-3. Figure 33 shows the construction, strata type and thickness, and the location and depth of MH-26 in relation to well W-3. The disturbance of the ground during the construction and installation of MH-26 and the brittle, fractured nature of shale, which is the dominant strata type, could also be contributing factors to an avenue for deep seated gas to escape and migrate.

Soil zone head space CO_2 gas: The collection of data from the soil zone wells began in May 2011 and continued for the duration of the study period. Figure 34 below shows the average monthly data through time compiled during the study period. The average monthly data are based on data collected during the course of each calendar month; the data collected each month varies from two to nine measurements.

Figure 34: Monthly average head space $\text{CO}_{2(g)}$ concentrations through time. Shallow soil zone monitoring wells W-2A, W-2D, W-3A, and W-6 are within the confines of the test site square, while W-1A and W-4/4A are on/near the boundaries of the test site square. The control wells are W-5 and W-7, which are east and west of the test site square respectively.

The peak and valley nature of the Figure 34 graph is indicative of biogenic $\text{CO}_{2(g)}$ fluctuation with the season; higher temperatures mean more microbial and plant root activity, thus raising the natural $\text{CO}_{2(g)}$ concentration of the soil zone. The annual discrepancies between mid-summer 2011, mid-summer 2012, and mid-summer 2013 could be due to natural seasonal fluctuations in temperature and precipitation that influence biogenic activities, to the microseepage of injected $\text{CO}_{2(g)}$, or to some combination thereof. Without any type of soil zone gas pre $\text{CO}_{2(g)}$ injection background data for each specific well, it may be impossible to differentiate the two.

Figure 35 illustrates a comparison of the monthly average head space CO_{2(g)} concentrations of two test site wells, W-2A and W-2D, and one control well, W-5 through time vs. the monthly average bore pressure of CO_{2(g)} injection wells MH-18 and MH-20 (located in the center of the test site square). W-2A and W-2D are located near the center of the test site square and near the stream on the 100 year flood plain at an elevation of ~916 ft. Control well W-5 is located well east of the eastern most boundary of the test site square along the test site access road away from, but near an ephemeral tributary of Fish Creek at an elevation of ~1069 ft. The floras near the three wells are a mix of perennial grasses, deciduous shrubs, and mature deciduous trees.

Figure 35: Monthly average head space $\text{CO}_2(\text{g})$ concentrations in wells W-2A and W-5 vs. the $\text{CO}_2(\text{g})$ injection bore gauge pressures in wells MH-18 and MH-20 through time.

The exact locations of wells W-2A, W-2D, and W-5 can be found in Figure 4 above. The variation in the data among years for the same season type could theoretically be a result of natural annual seasonality differences, the microseepage of injected $\text{CO}_2(\text{g})$, or a combination of the two. The fluctuation in the data collected at well W-5 should be due to natural annual seasonality differences only, as the well is located ~1.0 mile from the center of the test site square. The fluctuations in wells W-2A and W2D are maybe due to a combination of natural annual seasonality differences and the microseepage of injected $\text{CO}_2(\text{g})$. Well W-2A and W-2D are located in the center area of the test site square and have a significantly higher % $\text{CO}_2(\text{g})$ than

the control well W-5 during peak injection periods for July periods and especially for winter periods.

Table 15 shows the percent difference for soil CO_{2(g)} concentration between control well W-5 and the test site center shallow soil zone monitoring wells W-2A and W-2D. The percent difference was calculated using the following equation:

$$\% \text{ difference} = \frac{(\%W_{ts} - \%W_c)}{\%W_c} * 100\% \quad (13)$$

Where: %W_{ts} is a test site shallow soil zone well value (% CO_{2(g)}).

%W_c is the control shallow soil zone well (W-5) value (% CO_{2(g)}).

	July 2011	July 2012	July 2013	December 2011	December 2012	February 2012	February 2013	February 2014
W-2A Average Monthly (% CO_{2(g)})	8.07	3.85	7.27	4.27	2.68	3.03	1.92	2.55
W-2D Average Monthly (% CO_{2(g)})		7.21	11.1		1.67	2.90	1.89	2.54
W-5 Average Monthly (% CO_{2(g)})	4.59	2.55	3.35	0.52	1.01	1.07	0.87	0.35
% Difference W-2A/W-5	76	51	117	721	165	183	121	629
% Difference W-2D/W-5		183	231		65	171	117	626

Table 15: Average monthly CO_{2(g)} concentrations, in volume percent units, of shallow soil zone monitoring wells W-2A and W-2D, located in the center of the test site square, and shallow soil zone monitoring control well W-5, located ~1.0 miles SSE from the center of the test site square.

Control well W-5 represents natural, undisturbed conditions, with the areas around wells W-2A and W-2D, and well W-5 being similar in nature with deciduous trees and short perennial grasses. Table 15 shows that the percent difference between the control well and center test site wells is greater during a period of active automated CO_{2(g)} injection (July 2011 and July 2013) than during a period of very sporadic manual CO_{2(g)} injection (July 2012) that was preceded by an extended lull in CO_{2(g)} injection activities.

The greatest variations in the data occur during or just after sustained CO_{2(g)} injection activities and during a winter time when biogenic activity is at minimal levels. Data collected in

the head space of W-2A during the month of December 2011 show a variation in data between wells (W-2A/W-5) of 721%. The average head space CO_{2(g)} concentration of control well W-5, during December 2011 at 0.52%, represents normal soil concentrations for that time period.

Data collected in the head space of W-2D during the month of February 2014 show a variation in data between wells (W-2D/W-5) of 626%. The average head space CO_{2(g)} concentration of control well W-5, during February 2014 at 0.35%, represents normal soil concentrations for that time period. It is important to note the CO_{2(g)} concentration values found in wells W-2A and W-2D during February 2012, 2013, and 2014 do not vary considerably (between wells, within the same year and month), while the CO_{2(g)} concentration values measured within these wells during July 2012 and 2013 do vary considerably (between wells, within the same year and month). The higher CO_{2(g)} concentration for the head space of wells W-2A and W-2D during July 2013 and 2012 may be associated with the increase in CO_{2(g)} injection pressure during July 2013 (Figure 35 above), although higher CO_{2(g)} concentration is expected during the warm (summer) months.

A statistical correlation analysis using average monthly psig bore pressure in MH-18, vs. average monthly head space CO_{2(g)} concentrations in W-2D is shown in Figure 36, below. The data trend there reveals a high correlation coefficient or R-value indicating a significant positive data trend at 0.01 α , for a 12 month base lag in prior CO_{2(g)} injection pressure. The generated R²-value indicates 57% of the data may be attributed to the microseepage of injected CO_{2(g)}; the monthly correlation with CO_{2(g)} injection well MH-20 for the same 12 months lag period yielded very similar results at 59% reliability (Figure 37 below).

Figure 36: Determination and correlation coefficients (R^2 and R respectively) of pounds per square inch at the gauge (psig) of CO_{2(g)} injected into well MH-18 versus the average head space CO_{2(g)} concentration of shallow soil zone head space gas in monitoring well W-2D. The R value is significant at 0.01 α ; the R^2 value shows 57.5% of the data can be attributed to the regression trend based on a 12 month lag for prior CO_{2(g)} injection pressure.

Figure 37: Determination and correlation coefficients (R^2 and R respectively) of pounds per square inch at the gauge (psig) of $\text{CO}_{2(g)}$ injected into well MH-20 versus the average head space $\text{CO}_{2(g)}$ concentration of shallow soil zone head space gas in monitoring well W-2D. The R value is significant at 0.01 α ; the R^2 value shows 59% of the data can be attributed to the regression trend based on a 12 month lag for prior $\text{CO}_{2(g)}$ injection pressure.

Isotope data analysis of Bethany Meier: WVU graduate student Bethany Meier tested the applicability of using carbon stable isotopes to monitor for potential geologically sequestered $\text{CO}_{2(g)}$ leakage at the test site for August 2013 – August 2014 (Meier, 2014).

Figure 38 below shows a cross section, close up view of a typical shallow soil zone gas monitoring well. The customized cap was developed to accommodate three types of data collection; active (ball valve), diffusion (hypodermic needle), and direct (compression cap). The gas samples collected by Meier (2014) for isotopic analysis used the diffusion method by placing the hypodermic needle through the septum of a septum fitted vial.

The stable carbon isotope analysis done by Bethany Meier in conjunction with $\text{CO}_{2(g)}$ sequestration activities revealed no sequestered $\text{CO}_{2(g)}$ in the shallow soil zone wells, the shallow ground water wells, and the PBC via $\text{CH}_{4(g)}$ production well MH-12 (Meier, 2014).

Figure 38: Close up of a typical shallow soil zone gas monitoring well. A septum fitted vial is placed on the hypodermic needle, which is connected to a length of plastic tubing in order to collect a head space gas sample via diffusion.

Although an isotopic analysis of the shallow soil zone gas monitoring wells failed to show any isotopic signatures of injected $\text{CO}_{2(g)}$, this does not necessarily rule out $\text{CO}_{2(g)}$ microseepage, as the isotope collection methods may have been flawed. The interior portion of the hypodermic needle apparatus is connected to a length of plastic tubing, which extends to within the screened interval; the flaws in this method are with the assumptions that must be made. Does the plastic tubing extend to the screened interval; are there any kinks/obstructions within the plastic tubing; does the plastic tubing allow diffusion along its length; are lighter gases

or lighter isotopes of $\text{CO}_{2(g)}$ corrupting the data; is the well itself airtight to the extent where the diffusion process is only collecting head space gases; are these specific gases capable of flowing through the length of the plastic tubing; was the collection vial left in place long enough to allow for sufficient gas exchange (~30 minutes)? The carbon isotope analysis of the shallow soil zone wells may be compromised by the factors described above; therefore, there are too many unknowns with the head space $\text{CO}_{2(g)}$ isotope analysis to definitively state no microseepage of injected $\text{CO}_{2(g)}$ could have occurred.

The head space gas of the three test site shallow ground water monitoring wells was not analyzed by Meier (2014) for carbon isotopes; only the dissolved CO_2 content of the ground water was. The lack of CO_2 isotopic signatures by Meier (2014) in the ground water is not surprising, being that well W-1 is upslope of the $\text{CO}_{2(g)}$ injection system, well W-2 penetrates confining layers, and well W-3 also penetrates confining layers, but with 11 feet (upward from the surface of the water table) of the lower vadose zone exposed (uncased) to the well bore of well W-3.

Well W-3 shows the most distinct direct relationship between head space $\text{CO}_{2(g)}$ concentration and $\text{CO}_{2(g)}$ injection activities (Figure 41 below). Sequestered $\text{CO}_{2(g)}$ could conceivably migrate laterally into the head space of well W-3 through the exposed lower vadose zone, without making contact with ground water; gases migrate via the path of least resistance.

Figure 39 below shows the average % volume $\text{CO}_{2(g)}$ concentration values of all data collected in each of the shallow soil zone monitoring wells during the study period. The averages for wells W-1A, W-2A, W-3A, W-4/4A, and W-5 are based on 33 data points each. The average for wells W-2D and W-7, which were installed nine months after the other wells, are based on 24 and 25 data points respectively.

Figure 39: Average head space CO_{2(g)} concentrations incorporating all data points in each active shallow soil zone monitoring during the study period. Horizontal distance is not to scale.

Considering the landscape of the area, the shallow CO_{2(g)} concentrations should not vary significantly among the shallow soil zone monitoring wells, when in fact they do. Figure 40 below shows the location of the shallow soil zone monitoring wells in relation to the center and boundaries of the test site square.

Figure 40: Aerial view of the Marshall county test site and the locations of the shallow soil zone monitoring wells; the center, and eastern and western boundaries of the test site square; and the average (of all collected data) for shallow soil zone CO_{2(g)} % volume concentrations.

The highest shallow soil zone CO_{2(g)} concentrations were consistently observed in the test site center shallow soil zone wells, W-2A and W-2D. The CO_{2(g)} concentration data show an inverse relationship with distance from the center of the test site square, with the lowest overall values observed in the southeastern most (W-5) and northwestern most (W-7) shallow soil zone control wells. It is important to note, the CO_{2(g)} concentration data decrease proportionally in each direction from either W-2A or W-2D. The top right corner of Figure 40 above shows the average of all recorded CO_{2(g)} concentration values during the study period. Applying Equation 11 above, using the average total CO_{2(g)} concentration of W-2A and W-2D as the center test site wells, and the average total CO_{2(g)} concentration of W-5 and W-7 as the control wells, the percent difference is 102% for the length of the study period; this indicates the center test site wells have twice the CO_{2(g)} content of the distinct control wells. When the same comparison is

made using the average total CO_{2(g)} concentration of the southeastern and northwestern boundary shallow soil zone test site control wells, W-4/4A and W-1A, the percent difference is 81% for the length of the study period; this indicates an 81% higher CO_{2(g)} content for the center test site wells.

Water well head space CO₂ gas: The monitoring of the head space CO_{2(g)} concentration of the three test site ground water monitoring wells began in April of 2009 and ended in March of 2014.

Figure 41 shows the average monthly head space CO_{2(g)} gas concentration of each of the three test site shallow ground water monitoring wells, and the average monthly psig bore pressure of the two CO_{2(g)} injection wells through time, as well as the maximum hydrostatic pressure of the two underlying major coal beds.

Figure 41: Monthly average head space $\text{CO}_{2(g)}$ concentrations in shallow ground water monitoring wells W-1, W-2, and W-3 vs. the $\text{CO}_{2(g)}$ injection bore gauge pressures of MH-18 and MH-20 through time.

The average monthly values during summer growing season one in 2009, the background year prior to any $\text{CO}_{2(g)}$ injection, in Figure 41 above, show very low concentrations of head space $\text{CO}_{2(g)}$ and very little variation in the data from month to month and well to well. Table 16 below compares the average head space $\text{CO}_{2(g)}$ data of five full growing seasons and the percent increase in $\text{CO}_{2(g)}$ concentration from the background of 2009 for subsequent years, as defined by equation 14. The growing season is defined as the beginning of May to the beginning of October within the same calendar year. Growing season one (2009) head space $\text{CO}_{2(g)}$ values predate any $\text{CO}_{2(g)}$ injection activities and are assumed background levels. $\text{CO}_{2(g)}$ injection during growing season two (2010), for the most part, was sporadic, when 24 hour automated

bore pressures were generally less than 900 psig. During growing season three (2011), CO_{2(g)} injection was nearly continuous at bore pressures often greater than 900 psig. Growing season four (2012) started with the very sporadic manual injection of CO_{2(g)} with the system back to sustained automated CO_{2(g)} injection at bore pressures greater than 900 psig near the end of July 2012. Permission was granted by the West Virginia Department of Environmental Protection to CONSOL Energy Inc. to increase the CO_{2(g)} injection pressure; the pressure increase began at the end of June 2013 and ran until the beginning of September 2013. The injection pressure was increased in only one of the injection wells, MH-18, which had an average pressure during this time period of 1183 psig.

$$\% \text{ increase} = \frac{\text{CO}_2(g) \text{ (volume \%)} - \text{background CO}_2(g) \text{ (volume \%)}}{\text{background CO}_2(g) \text{ (volume \%)}} * 100\% \quad (14)$$

Average Head Space CO_{2(g)} Concentration (volume %) and Concentration Increase from Background (%)	W-1	W-2	W-3
Growing season 1 (2009 background)	0.056	0.059	0.056
Growing season 2 (2010)	0.098	0.161	0.166
Growing season 3 (2011)	0.139	0.133	0.449
Growing season 4 (2012)	0.145	0.153	0.222
Growing season 5 (2013)	0.118	0.116	0.246
Volume % increase from background (2010)	75	173	196
Volume % increase from background (2011)	148	125	702
Volume % increase from background (2012)	159	159	296
Volume % increase from background (2013)	111	97	339

Table 16: Growing season average head space CO_{2(g)} concentrations in wells W-1, W-2, and W-3 and the percent head space CO_{2(g)} concentration increase from background during subsequent growing seasons (where growing season is defined from beginning May to beginning October).

Figure 42 below represents well W-3 and the conditions in the subsurface. The three test site ground water monitoring wells are constructed identically, except as previously mentioned the lower vadose zone is exposed to the permeable bore liner in well W-3 due to the length of the

casing (20 feet below the ground surface) and the average depth of the water table (31 feet below ground surface).

Figure 42: Cross section of test site ground water monitoring well W-3 where the water table is situated below the casing bottom which exposes gases of the lower vadose zone to the well. The green interval represents the plastic screen liner.

Although the lower vadose zone is exposed in well W-3, it is unlikely the exposure is solely responsible for the 702% increase in $\text{CO}_{2(g)}$ during 2011 (Table 16) from background levels observed in growing season three (2011) solely via the downward transport of soil CO_2 . The evidences against it are: the background (2009) head space $\text{CO}_{2(g)}$ concentration in all three wells is nearly the same; a significant increase from background (2009) occurred once injection

activities commenced; the overall upward trend in the data collected in wells W-1 and W-3; and how the trend in well W-3 has a distinct direct relationship with the length (duration) of CO_{2(g)} injection activities.

Perfluorocarbon tracers: Perfluorocarbon (PFC) tracers were injected by Arthur Wells and J. Rodney Diehl of USDOE NETL into CO_{2(g)} injection wells MH-18 and MH-20 over a seven day period, April 15-22, 2011.

The PFC tracer analysis from the weekly collection of head space gas from CH_{4(g)} production wells MH-11 and MH-12 revealed the following: ~200 days for the PMCH tracer to migrate from injection well MH-20 to production well MH-11; ~180 days for the PTCH tracer to migrate from injection well MH-18 to production well MH-11; and ~7 days for the PTCH tracer to migrate from injection well MH-18 to production well MH-12. Figure 3 above shows the injection well locations relative to the production wells where the PFC tracer was detected. See Figure 43 below for detected PFC tracers in CH_{4(g)} production wells versus time.

Figure 43: PTCH and PMCH tracer detection at production wells MH-11 and MH-12 at the number of days from the start of tracer injection.

The PMCH tracer injected into south and east facing CO_{2(g)} injection well MH-20 (Figure 2), detected in production well MH-11, had migrated ~1540 feet in a SSE direction in ~200 days, while the PTCH tracer injected into west and north facing CO_{2(g)} injection well MH-18, detected in well MH-11, had migrated ~1740 feet in a SSE direction in ~200 days (Figure 43). The length of time elapsed from PFC injection to PFC detection is reasonable at both injection/production wells considering the orientation of the subsurface strata as described in the introduction.

Correlation coefficients were calculated based on two variables: total weekly tons of CO_{2(g)} injected, and femtograms per liter (fg/L) of the detected PFC tracer; the PFC tracer values were correlated with the total tonnage of CO_{2(g)} injected into, and the pressure in psig of each of the CO_{2(g)} injection wells MH-18 and MH-20. The CO_{2(g)} injection lag times were varied from 0

to 50 weeks (350 days) for the regression analyses, with the most significant correlation trends, at 0.01 α , chosen for display in Table 17 and Table 18 below.

Tracer Type	Injected Via	Correlation Variable	MH-11 Correlation %	Days Lag
PTCH	MH-18	Tons inj.	87.6	308
PMCH	MH-20	Tons inj.	67.7	217

Table 17: Regression analysis based on mass of CO_{2(g)} injected with the CO_{2(g)} injection lag time, where the R value is most significant at 0.01 α . The R² value indicates the correlation percentage of the data attributed to the regression trend.

Tracer Type	Injected Via	Correlation Variable	MH-11 Correlation %	Days Lag
PTCH	MH-18	psig	69.5	308
PMCH	MH-20	psig	71.9	280

Table 18: Regression analysis based on CO_{2(g)} injection pressure with the CO_{2(g)} injection lag time, where the R value is most significant at 0.01 α . The R² value indicates the correlation percentage of the data attributed to the regression trend.

Table 17 shows the most significant, at 0.01 α , positive correlations for both PTCH and PMCH versus weekly total CO_{2(g)} tonnage injected and Table 18 shows the most significant, at 0.01 α , positive correlations for both PTCH and PMCH versus weekly average CO_{2(g)} psig. The lag times coinciding with the most significant correlation percentages align with the actual detection times displayed in Figure 43 above. Although the PTCH tracer was detected in production well MH-12, which taps the PCB ~600 feet above where the PFC tracers were injected, there are no significant positive correlations within the time span of significant detectable PTCH tracer (~4 weeks) and the indicated lag time is three weeks (21 calendar days) prior to peak PTCH detection. No PMCH tracer, which was injected into MH-20, was detected in CH_{4(g)} production well MH-12 for the PCB. The UFCB is located ~600 feet below the PCB with confining layers between the formations (Figure 33). The horizontal distance from the test

site center to the pump jack MH-12, which penetrates the PCB, is ~1740 feet. Compared to the short amount of time elapsed to peak PTCH tracer detection in well MH-12, the results displayed in Figure 43 were not expected due to distances of migration versus time. The installation of access well MH-19 and the subsequent plugging attempts could have contributed to the rapidly escaping PTCH tracer observed in well MH-12.

Figure 44 represents a map view and Figure 45 represents a cross sectional view of the CO_{2(g)} injection apparatus in the center of the test site square. The schematics of the cross section in Figure 45 are based on technical and progress reports by Ravi Srivastava of CONSOL Energy Inc.

Figure 44: Map view of the center of the test site square and where the CO_{2(g)} injection system is located.

Figure 45: Cross sectional view of the subsurface facing north. The schematic is a representation of the suspected avenues of leakage of PTCH tracer into the PCB 500 feet to 600 feet above the repository UFCB. A' red vertical to the horizontal transition was the first and second cement plugging attempts of MH-19, the green offshoot from A' was the third cement plugging attempt of MH-19, and A⁰ was the fourth and final cement plugging attempt of MH-19.

During the first attempt to plug access well MH-19 (Figure 45) in 2009, a section of the uncased bore near where it transitions from the vertical to the horizontal, experienced continuous cave-ins, which forced operations to be suspended until a proper correction plan could be implemented (Srivastava R. S., 2009).

A second attempt to plug access well MH-19 (Figure 45) was made by using drill pipe in lieu of tubing for air and foam circulation, with stiff foam being used to reduce cave-ins. In the process of retracing the original, collapsed well bore, the directional drillers became sidetracked and started an offshoot bore; the sidetrack was plugged and another attempt at retracing the

original access commenced. At a depth from the ground surface of ~1190 feet, the drill string encountered an apparent washout cavity preventing the string from following the original curve; operations were then suspended (Srivastava R. S., 2009).

A third attempt, shown in Figure 45, was made to plug the original access well MH-19 from the washout depth of ~1180 feet where a packer was set, then cemented the entire reachable length to ~1060 feet below the surface for a kick off point for a new sidetracked curve. The sidetrack curve was to bypass the cavity by going forward of it and reentering the original access well along the horizontal length. The attempt fully intersected the original horizontal access well and created a new horizontal bore parallel to the original access bore. The new horizontal length dead-headed into the coal and did not intersect the horizontal segment of well MH-19; therefore it was filled with a volume of cement to ~200 feet into the casing and abandoned (Srivastava R. S., 2009).

A fourth and final attempt to plug the original access well MH-19 was made by drilling a new vertical access well, MH-19-1A (Figure 45), at the exact point where MH-19 enters the UFCB (Srivastava R. S., 2009). Once the UFCB was encountered and entered, a hole opening tool was lowered into the bore to expand the diameter of the well in the UFCB to about six feet; the expansion of the bore would ensure communication with access well MH-19. The final step was to pump a volume of cement down the bore to plug the new access well, including the expanded section.

A mechanical integrity test of the cement plug (Figure 44) was conducted by filling the annulus zone between the injection tubing and injection well casing of CO_{2(g)} injection well MH-18 (Figure 45) with water, pressurizing the annulus zone from 1050 psig to 1400 psig, and monitoring the annular pressure for 30 minutes. The mechanical integrity test was conducted on

August 6, 2009 with no loss of annular pressure observed. Therefore the underground injection control (UIC) permit was issued by WVDEP on August 18, 2009 (personal communication with CONSOL Energy Inc. personnel).

The PTCH tracer was first detected in PCB CH_{4(g)} production well MH-12 seven days after this tracer injection began into well MH-18; see Figure 3 for the well geometrics. The most likely scenario as to how the PTCH tracer migrated ~600 feet vertically upwards from the UFCB into the PCB involves: the partial plugging of access well MH-19 via MH-19-1A and the cave-ins and washout encountered while attempting to plug access well MH-19 on three separate occasions; the general eastern dip direction of the strata at the specified depths; and the podded, wet nature of the UFCB where injection well MH-18 penetrates it.

The mechanical integrity test of CO_{2(g)} injection well MH-18 after cement plugging, as discussed earlier, was conducted for 30 minutes at pressures between 1050 psig and 1400 psig with no decrease in annular pressure observed; i.e. the partial plugging of access well MH-19 had appeared to work. On September 8, 2009 the first CO_{2(g)} injection activities began; this was also the first day the injection wells, MH-18 and MH-20, became pressurized with CO_{2(g)}. They remained pressurized until the conclusion of the study. As of the end of January 2014 when CO_{2(g)} injection ceased, injection well MH-18 had been pressurized for 2,324,160 minutes (4.42 years) at an average (of the monthly averages) pressure of 764 psig. At the time of PTCH tracer injection, injection well MH-18 had been pressurized for 809,978 minutes (1.54 years) at an average (of the monthly averages) pressure of 664 psig. Although the average pressure at the time of PTCH tracer injection was less than half the high end pressure (1400 psig) of the mechanical integrity test, the duration of the mechanical integrity test was 0.0037% of the length of time the bore had been pressurized at the time of said PTCH tracer injection; therefore this

integrity test may not have been sufficient in duration to make any significant predictions for injected gas migration.

The duration of time and the constant pressure could have catalyzed some failure of the partial plug and/or weakened strata, allowing access to the overlying strata near the areas of bore failure and/or the washout cavity where the PTCH tracer could have gained access to the PCB. Once such access was gained, the PTCH tracer would have continued to migrate along the path(s) of least resistance, whether they were borehole or natural fracture avenues. Considering the trend of the strata and the wet, porous nature of the PCB and adding to that the pressure differential generated by the nearly continuous running of the pump jack at CH_{4(g)} production well MH-12, the vertical pressure gradient (as discussed earlier) of the PCB, and the slippery nature of the tracer molecule, it is highly likely the PTCH tracer could have traveled the vertical and horizontal distances, 500 to 600 feet and 1740 feet respectively, in the length of time elapsed from tracer injection to tracer detection in well MH-12, which was about seven days.

Conclusions

Stream water chemistry: The environmental monitoring of Fish Creek (Figure 4) took place from October 2008 until June 2013. The natural stream water chemistry is slightly basic ($\text{pH} > 7.00$ S.U.) and predominately $\text{Ca}^{2+}_{(\text{aq})}$ and $\text{HCO}_3^{-1}_{(\text{aq})}$ with very little variation in dissolved ion content among stream sampling point locations through time. The ionic composition of the stream water is defined by the strata it and its tributaries cut through within the watershed, which are composed of Permian age alternating beds of sandstone, shale, and minor limestone. The ionic concentrations are inversely dependent on discharge, with lower concentrations observed during the wet (winter/spring) season and during storm events, and higher concentrations observed during the dry (summer/fall) season. The local test site ground water runoff area is extremely small compared to the overall drainage basin of the Pennsylvania Fork of Fish Creek, and therefore the dilution effect of the stream water on test site ground water runoff is too great to affect stream water chemistry except when large slugs of local concentrated contamination occur. The only anomaly observed in the stream water chemistry was at the onset of the study during late 2008 when significant brine contamination was observed from the suspected illegal dumping of coal bed formation water at the site of the former formation water holding tanks. No other environmental chemical impacts to stream water were identified as a result of $\text{CO}_{2(\text{g})}$ injection or $\text{CH}_{4(\text{g})}$ extraction.

Natural ground water chemistry: The chemistry of the regional ground water in drilled wells greater than 20 feet in depth varies to some extent throughout the area (Figure 4). The western control, B-type domestic water supply wells near Bellton show the lowest pH of any drilled well, with the average pH being 7.09 S.U. in domestic well B-1 and 7.24 S.U. in domestic well B-2. The average electrical conductivity for the B-type wells was 788 $\mu\text{S}/\text{cm}$ for domestic

well B-1 and 794 $\mu\text{S}/\text{cm}$ for domestic well B-2. The major cation in domestic well B-1 was Ca^{2+} with an average value of 73.5 mg/L, while the major cation observed in domestic well B-2 was Na^{1+} with an average value 99 mg/L. The major anion in both of the B-type wells was HCO_3^{1-} with an average value of 263 mg/L in domestic supply well B-1 and 365 mg/L in domestic well B-2. No known environmental chemical impacts occurred to the Bellton wells as a result of $\text{CO}_{2(g)}$ injection or $\text{CH}_{4(g)}$ extraction at the test site.

The only somewhat reliable control for shallow ground water in the eastern Georgetown area is domestic supply well G-1, which displays the least number of physical setting unknowns associated with the water chemistry. The average pH observed was 8.56 S.U. with an average electrical conductivity of 467 $\mu\text{S}/\text{cm}$. The major cation observed was Na^{1+} with an average value of 103 mg/L. The major anion observed was HCO_3^{1-} with an average value of 279 mg/L.

Another shallow ground water control well in the Georgetown area to the east of the test site, domestic supply well G-4, is of little use for comparison purposes with test site wells due to the physical setting unknowns associated with it, mainly the nature of installation, the cased interval, and the avenues for surface contamination; therefore, data for domestic supply well G-4 were not used for the study. The data for two remaining Georgetown area domestic water supplies were not useful for the comparison purposes with test site wells of this study, as G-3 is a hand dug well 20 feet deep with a hand pump for water extraction, and G-2 is a spring source, located on the ridge ~0.80 miles to the SW of the source; both of the supplies do not represent bedrock aquifers typical of the test site. No known contamination occurred to these Georgetown area water supplies as the result of $\text{CO}_{2(g)}$ injection or $\text{CH}_{4(g)}$ extraction at the test site.

The average shallow ground water chemistry at the test site varies with location for monitoring wells W-1, W-2, and W-3. The average pH and electrical conductivity observed for

these 105 feet deep wells during the study period (Oct. 2008 – Oct. 2013) were: 8.39 S.U. and 1105 $\mu\text{S}/\text{cm}$ in W-1, 8.70 S.U. and 634 $\mu\text{S}/\text{cm}$ in W-2, and 9.28 S.U. and 829 $\mu\text{S}/\text{cm}$ in W-3. The major cation and anion in these three wells were Na^{1+} and HCO_3^{1-} respectively. The average concentrations observed were 171 mg/L Na^{1+} and 298 mg/L HCO_3^{1-} in well W-1, 127 mg/L Na^{1+} and 184 mg/L HCO_3^{1-} in well W-2, and 199 mg/L Na^{1+} and 449 mg/L HCO_3^{1-} in well W-3.

Contaminated ground water chemistry: The chemistry of the Georgetown area domestic supply well G-3 shows contamination, influenced to a great extent by rainwater and rainwater runoff over agricultural grazing land and septic leachate as is indicated by the acidic pH (~5.60 S.U.), the abnormally high $\text{K}^{1+}_{(\text{aq})}$ concentration of 12.7 mg/L versus 0.1 – 2.2 mg/L from all other water sources, and the high $\text{NO}_3^{1-}_{(\text{aq})}$ concentration of 27.2 mg/L as nitrate nitrogen versus non-detectable (ND) – 1.2 mg/L from all other water sources. Well G-3 has caused two suspected cases of Blue Baby Syndrome and is likely to contain elevated levels of fecal coliform and E. Coli bacteria based on $\text{NO}_3^{1-}_{(\text{aq})}$ concentration. The property owners of well G-3 were consulted about the pollution, its likely sources, its health effects, a simple solution for the suspected bacteria problem, and a more costly solution for the high $\text{NO}_3^{1-}_{(\text{aq})}$ concentration. Contaminated ground water of well G-3 may continue to pose a risk to human health if remedial actions are not taken regarding the extreme nitrate contamination.

The elevated cation ($\text{Na}^{1+}_{(\text{aq})}$ and $\text{Ca}^{2+}_{(\text{aq})}$) and anion ($\text{Cl}^{1-}_{(\text{aq})}$) concentrations observed in shallow ground water of monitoring well W-1, relative to control well G-1, were most likely the result of the water pump jack seal failure in nearby coal bed production well MH-12 (Figure 2) on the test site. Production well MH-12 was actively producing coal bed $\text{CH}_{4(\text{g})}$ before injection activities and environmental monitoring began; therefore it is likely that seal failure was an ongoing problem which was not corrected until it was brought to the attention of the CCS/ECBM

recovery project head. Over time, if pump jack seal failure was the sole cause of this ground water pollution, the excess ions would have been flushed from the aquifer system; however ion concentrations remained elevated or only decreased slightly over time, so other potential contamination sources may be from the production bore, i.e. bore and/or casing failure, grout failure within the annulus zone, a different source, or natural softening within the zone of saturation. Pump jack seal failure was a reoccurring problem during the study period.

The elevated $\text{Na}^{1+}_{(\text{aq})}$ and $\text{Cl}_{(\text{aq})}^{1-}$ concentrations (relative to control well G-1) in the shallow aquifer for monitoring well W-2, located at the center of the test site square, most likely were a result of the same pollution event observed at Fish Creek stream locations S-2 and S-3 that occurred in Fall 2008. The length of time and the volume of formation water disposed of via the slight valve opening of the formation water holding tanks would have infiltrated the aquifer via percolation through the soil zone. The physical properties (low permeability shale) of the aquifer for well W-2 indicate it could take a substantial length of time for a pollution event to flow and be flushed through the system. A slight upward trend over time was observed in the EC data collected for monitoring well W-2, especially during periods of automated $\text{CO}_{2(\text{g})}$ injection, which could perhaps indicate slight chemical weathering via $\text{CO}_{2(\text{aq})}$ due to slight microseepage of injected $\text{CO}_{2(\text{g})}$ into the fresh water zone and the subsequent dissolution of ions from the strata.

The chemistry of the ground water extracted from the aquifer of monitoring well W-3, located on the west side of the test square, is due to $\text{CH}_{4(\text{g})}$ contamination from a deep seated origin in both the aqueous phase, as indicated by the geochemical signatures, and in the gas phase as indicated by the head space percent volume concentrations. Geochemical signatures indicate well W-3 has been contaminated with $\text{CH}_{4(\text{aq})}$ since environmental monitoring began in

early October 2008. The observed increase in CH_{4(g)} head space concentration could have been a result of or aggravated by: the additional volume of gas being injected into the UFCB; the potential formation pressure change of the UFCB versus hydrostatic pressure; the insufficient amount of or failure of grouting material used in nearby deep monitoring well MH-26; the exposed lower vadose zone within well W-3 being the path of least resistance for the lateral flow of CH_{4(g)}; or some combination thereof. The W-3 head space CH_{4(g)} data had the highest concentrations observed near the end of and for approximately one year after the longest period of sustained, automated CO_{2(g)} injection.

Vadose zone CO_{2(g)} chemistry: The head space CO_{2(g)} concentrations of the three test site ground water monitoring wells (Figure 4) show a significant increase, usually over 100%, from pre CO_{2(g)} injection levels, with well W-3 having the most significant change with a ~702% increase from pre CO_{2(g)} injection levels and a distinct trend coinciding with the duration of automated CO_{2(g)} injection activities. As is the case with CH_{4(g)} in well W-3, the exposed lower vadose zone would offer the path of least resistance to the surface if sequestered CO_{2(g)} migrated vertically through the water table and began to migrate laterally through bedding plane partings, fractures, and pore spaces.

Without pre CO_{2(g)} injection background data for the shallow soil zone monitoring wells (Figure 4), it is impossible to know the effects, if any, CO_{2(g)} sequestration had on the shallow vadose zone. However, high CO_{2(g)} concentration values were observed in the test site center shallow soil zone monitoring wells. Seasonality can explain the peak and valley nature of the head space CO_{2(g)} concentrations of the shallow soil zone gas monitoring wells. Higher CO_{2(g)} concentrations were observed in the warm season (mid-spring to mid-fall), when soil microbe and plant photosynthesis activities are the greatest, relative to the dormant season (mid-fall to

mid spring), when soil microbe and plant photosynthesis activities are the lowest. The greatest variation in $\text{CO}_{2(g)}$ data between the centrally located test site wells, W-2A and W-2D, and southeastern control well W-5 occurred during the winter season; well W-2A was 721% greater and well W-2D was 626% greater than well W-5 in $\text{CO}_{2(g)}$ vadose concentration on average. The significantly higher $\text{CO}_{2(g)}$ concentrations observed during winter within the test square center area may be due to the slight microseepage of sequestered $\text{CO}_{2(g)}$.

Carbon isotope analyses were conducted by Bethany Meier (Meier 2014) on ground water from the shallow ground water monitoring wells and on the vadose zone for the shallow soil zone monitoring wells from August 2013 to August 2014. Although no isotopic signatures of injected $\text{CO}_{2(g)}$ were observed in the ground water, microseepage may have occurred in the head space of shallow ground water monitoring well W-3 through the exposed (to the well bore) lower vadose zone via lateral migration, especially during 2011.

The lack of any isotopic signatures from the vadose zone head space of the shallow soil zone monitoring wells is possibly due to the passive method of collection as described above, the length of time the gas collection vial was left in place (~30 minutes), and the integrity of the internal portion of the gas exchange pathway.

Perfluorocarbon tracer interpretation: Two different types of PFC tracers were injected simultaneously, by USDOE-NETL personnel, with $\text{CO}_{2(g)}$ into each of the two test site center injection wells, MH-18 and MH-20 (Figure 2) from April 15 to April 22, 2011, then analyzed for in the head space gas of $\text{CH}_{4(g)}$ production wells MH-11 and MH-12 (Figure 2) over a period of 287 days. The time elapsed, from PMCH tracer injection into $\text{CO}_{2(g)}$ injection well MH-20 to PMCH tracer detection in the head space of $\text{CH}_{4(g)}$ production well MH-11, was ~200 days over a travel distance of ~2600 ft.; this is reasonable due to the eastern direction of the

subsurface CO_{2(g)} injection well laterals and their subsurface trend. The time elapsed, from PTCH tracer injection into CO_{2(g)} injection well MH-18 to PTCH tracer detection in the head space of production well MH-11, was ~200 days over a travel distance of ~2300 ft.; although the subsurface laterals of MH-18 are directed westerly, the length of time is reasonable due to flow barriers and the eastern dip of the subsurface strata, which could force the tracer eastward. The detection of PTCH tracer in the head space of production well MH-12 in the PCB was unexpected, and is most likely the result of the multiple attempts at plugging access well MH-19 (Figure 3) and the weakening/failure of portions of the subsurface strata and/or the failure of the cement plug, once plugging was successful, via a substantial increase in the pressure exerted on it over a great length of time.

The actual travel time, from injection well MH-18, to detection in production well MH-11 of the PTCH tracer, extended from 182 days to 287 days; this range also holds true for PMCH tracer detection in production MH-11, which was injected into injection well MH-20. The PFC tracer data after 287 days were not made available to the investigator, but it is a reasonable assumption that PTCH and PMCH tracers would have been detected in production well MH-11 at least through 308 days as per the correlation coefficients displayed in Table 17 and Table 18. The correlation coefficients reveal both tonnage of CO_{2(g)} injected and the injection pressure play a role in PFC tracer migration.

Overall findings: No significant environmental impacts were observed as a result of CO_{2(g)} injection or enhanced CH_{4(g)} production in the regional ground water, the test site surface stream water, the shallow vadose zone, and the shallow soil zone.

References

- Arkin, H., & Colton, R. R. (1963). *Tables for Statisticians*. New York: Barnes & Noble, Inc.
(Original work published 1950).
- Bromhal, G. S. (2004, May). *Assessing Economics for Sequestering CO₂ in Coal Seams with Horizontal Wells*. Presentation presented at the 3rd Annual Sequestration Conference, Alexandria, VA.
- Calderon, C. (2010). *Characterization and Simulation of ECBM: History Matching of Forecasting CO₂ Sequestration in Marshal County, West Virginia*. Unpublished doctoral dissertation, West Virginia University, Morgantown, WV.
- Drever, J. I. (1997). *The Geochemistry of Natural Waters* (3rd ed.). Upper Saddle River, NJ: Prentice-Hall, Inc. (Original work published 1982).
- Fetter, C. W. (2001). *Applied Hydrogeology*. Upper Saddle River, NJ: Prentice-Hall.
- Harrison, S. S. (May-June 1985). *Contamination of Aquifers by Overpressuring the Annulus of Oil and Gas Wells*. *Ground Water*, 23(3), 317-324.
- Harrison, S. S. (November-December 1983). *Evaluating System for Ground-Water Contamination Hazards Due to Gas-Well Drilling on the Glaciated Appalachian Plateau*. *Ground Water*, 21(6), 689-700.
- Hennen, R. V. & White, I. C. (1909). *County Reports and Maps; Marshall, Wetzel, and Tyler Counties*. West Virginia Geological Survey.
- Hega, B. D., Berry, K. E., & Rauch, H. W. (2011, October). *The Environmental Effects of Geologically Sequestered Carbon Dioxide Gas and the Enhanced Recovery of Coal Bed Methane from an Unminable Coal Seam*. Poster Paper presented at the Annual Meeting of The Geological Society of America, Minneapolis, MN.

- Johnston, J. H. (2009). *Affidavit of Plugging and Filling Well*. Charleston: State of West Virginia Department of Environmental protection.
- Kehew, A. E. (2001). *Applied Chemical Hydrogeology*. Upper Saddle River, NJ: Prentice-Hall, Inc.
- Kelly, W. R., Matisoff, G., & Fisher, J. B. (1985). *The Effects of a Gas Well Blow Out on Groundwater Chemistry*. Environmental Geology Water Science, 7(4), 205-213.
- Langmuir, D. (1997). *Aqueous Environmental Geochemistry* (1st ed.). Upper Saddle River, NJ: Prentice-Hall, Inc. (Original work published 1997).
- Locke, J. E., Winschel, R. A., Bajura, R. A., Wilson, T., Siriwardane, H. J., Gondle, R. K., Rauch, H. W., Hega, B. D., Mohaghegh, S. D. (2011, September). *CO₂ Sequestration in Unmineable Coal with Enhanced Coal Bed Methane Recovery: The Marshall County Project*. Proceedings Paper presented at the International Pittsburgh Coal Conference, Pittsburgh, PA.
- Meier, B (2014). *Using Stable Carbon Isotopes to Monitor for Potential Leakage of CO₂ at an Enhanced Coal Bed Methane Recovery Site in Marshall County, WV*. WVU geology thesis, Department of Geology and Geography, West Virginia University, Morgantown, WV.
- Rauch, H. & Hega, B. (2010). *Shallow Hydrogeologic Monitoring within the CONSOL Energy Inc. Pilot Test Site*. Internal WVU research report.
- Srivastava, R. S. (2009). *Proposal to Test the Effectiveness of the Partial Plugging of Access Well MH-19*. Internal CONSOL Energy Inc. report.

Srivastava, R. S. (November 2009), Semi-annual Progress Report by CONSOL Energy Inc. to USDOE. *Enhanced Coal Bed methane Production and Sequestration of CO₂ in Unmineable Coal Seams.*

Stumm, M., & Morgan, J. J. (1996). *Aquatic Chemistry* (3rd ed.) (J. L. Schnoor & A. Zehnder, Eds.). Hoboken, NJ: John Wiley & Sons, Inc.

Van Voast, W. A. (2003). *Geochemical Signature of Formation Waters Associated with Coalbed Methane*. AAPG Bulletin, 87(4), 667-676.

Winschel, R. A., Locke J. E., Srivastava, R. S., Bajura, R. A., Wilson, T., Siriwardane, H. J., Rauch, H. W., Patchen, D. G., Hega, B. D., Gondle, R. K., Wells, A. W. (2010, October). *CO₂ Sequestration in Unmineable Coal with Enhanced Coal Bed Methane Recovery: The Marshall County Project*. Proceedings Paper presented at the International Pittsburgh Coal Conference, Istanbul, Turkey.