**ANALYSIS OF DEVONIAN BLACK SHALES IN KENTUCKY FOR
POTENTIAL CARBON DIOXIDE SEQUESTRATION AND ENHANCED
NATURAL GAS PRODUCTION**

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Abstract

CO₂ emissions from the combustion of fossil fuels have been linked to global climate change. Proposed carbon management technologies include geologic sequestration of CO₂. A possible, but untested, sequestration strategy is to inject CO₂ into organic-rich shales. Devonian black shales underlie approximately two-thirds of Kentucky and are thicker and deeper in the Illinois and Appalachian Basin portions of Kentucky than in central Kentucky. The Devonian black shales serve as both the source and trap for large quantities of natural gas; total gas in place for the shales in Kentucky is estimated to be between 63 and 112 trillion cubic feet. Most of this natural gas is adsorbed on clay and kerogen surfaces, analogous to methane storage in coal beds. In coals, it has been demonstrated that CO₂ is preferentially adsorbed, displacing methane. Black shales may similarly desorb methane in the presence of CO₂.

The concept that black, organic-rich Devonian shales could serve as a significant geologic sink for CO₂ is the subject of current research. To accomplish this investigation, drill cuttings and cores were selected from the Kentucky Geological Survey Well Sample and Core Library. Methane and carbon dioxide adsorption analyses are being performed to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential. In addition, sidewall core samples are being acquired to investigate specific black-shale facies, their potential CO₂ uptake, and the resulting displacement of methane. Advanced logging techniques (elemental capture spectroscopy) are being investigated for possible correlations between adsorption capacity and geophysical log measurements.

Initial estimates indicate a sequestration capacity of 5.3 billion tons CO₂ in the Lower Huron Member of the Ohio shale in parts of eastern Kentucky and as much as 28 billion tons total in the deeper and thicker portions of the Devonian shales in Kentucky. Should the black shales of Kentucky prove to be a viable geologic sink for CO₂, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO₂ storage and enhanced natural gas production.

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Executive Summary

Increased emissions of CO₂, especially from the combustion of fossil fuels, are being linked to global climate change and are of considerable global concern. These concerns are driving initiatives to develop carbon management technologies, including geologic sequestration of CO₂. One option for sequestration may be Devonian black shales, organic-rich rocks that serve as both the source and trap for natural gas. Most of the natural gas is adsorbed on clay and kerogen surfaces, very similar to the way methane is stored within coal beds. It has been demonstrated in gassy coals that, on average, CO₂ is preferentially adsorbed, displacing methane at a ratio of two for one. Black shales may similarly desorb methane in the presence of adsorbing CO₂. If this is the case, black shales may be an excellent sink for CO₂ and have the added benefit of serving to enhance natural-gas production. A bibliography of Devonian shale has been compiled to identify previous work and provide supporting data for continued research.

Because of the volume of material lost during washing the sampling protocol has been modified to collect cuttings before washing. Unwashed candidate samples have been selected and are being prepared for total organic carbon (TOC), vitrinite reflectance ($R_{0 \text{ random}}$), and petrographic and CO₂ adsorption analyses to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential.

Measured CO₂ adsorption capacity ranges from 35 to 2,078 standard cubic feet CO₂ per ton of shale. The values representing the higher end of this range are problematic and the samples are being re-processed. Initial estimates indicate a sequestration capacity of 5.3 billion tons CO₂ in the Lower Huron Member of the Ohio shale in parts of eastern Kentucky and as much as 28 billion tons total in the deeper and thicker portions of the Devonian shales in Kentucky. Should the black shales of Kentucky prove to be a viable geologic sink for CO₂, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO₂ storage and enhanced natural gas production.

Introduction

Since the discovery of natural gas production from the Devonian shales of Kentucky between 1858 and 1865, these carbonaceous shales have constituted an important energy resource in Kentucky. Thick and deep sequences of shale exist in both the Illinois and Appalachian Basins (Figure 1). Greenhouse gases, CO₂ emissions in particular, are being linked to global climate change. If regulations are adopted that require limiting CO₂ emissions, disposal strategies must be identified. Using CO₂ flooding of coals as a model, the large component of adsorbed natural gas in organic-rich shales suggest that black shale might be an attractive sequestration target.

The project is concentrating on the Devonian Ohio shale of eastern Kentucky (Figure 2). This area is both the most active area (number of wells drilled over the past 5 years) and the most prolific natural gas producing area in the state accounting for 98 percent of Kentucky's gas production. The Kentucky Geological Survey maintains an extensive collection of cuttings recovered during oil and gas well drilling in the Well Sample and Core Library.

Figure 1. Map of the distribution of the Devonian shale in Kentucky, showing the occurrence of deeper and thicker shale with possibly greater potential for geologic sequestration of CO₂.

Figure 2. Map showing distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3)

Experimental

- 1) The sampling protocol has been modified to eliminate washing and air-drying of drill cuttings. Washing the samples resulted in the loss of too much material. In one case, a substitute for a selected well had to be chosen because insufficient material was available for sampling after washing. Eliminating air drying of the samples saves about one week per each well sampled.
- 2) Unwashed sets of recently acquired drill cuttings have been identified. These samples are being sorted and processed to place them in permanent storage bags and boxes.
- 3) The well sample data spreadsheet has been matched to the main oil and gas well record database in order to compile a GIS coverage of these data (**Figure 4**). The GIS was used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

Results and Discussion

Distribution and stratigraphy of the Devonian shale in eastern Kentucky suggest dividing well cuttings into up to three samples for adsorption analysis. The upper part of the shale from the Cleveland Member to the Middle Huron ("341OHIOU") is generally less organic-rich as indicated by the gamma-ray response on standard geophysical well logs (Figure 3). Drill cuttings of this sequence generally have a lighter gray color and more recognizable quartz material than the darker gray to black samples with sparse pyrite that are characteristic of the Lower Huron Member ("341HURNL"). In some areas of the Big Sandy Gas Field, the Olentangy and Rhinestreet members of the Ohio shale ("341OHIO") are present but have a somewhat lesser organic content. Where present, these shales will be composited as a separate sample. Some wells have an insufficient volume of cuttings available to analyze the individual members of the Ohio shale; these composite samples are designated "341OHIO."

A database of candidate Devonian shale wells for sampling was compiled. Kentucky statutes [KRS 353.660(2)] provide the Survey with the right to request well samples. In anticipation of this project, samples were requested for proposed Devonian shale penetrations in eastern Kentucky. Paper records of

well samples received were requested from staff of the well cuttings and cores repository and entered into an Excel spreadsheet. A total of 595 candidate wells have been identified (**Figure 4**). Geophysical logs from these wells are being scanned to assist in stratigraphic interpretation. A GIS will be used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

While processing unwashed and cataloged drill cuttings at the Well Sample and Core Library, several pallets of recently received, unwashed, but uncataloged, cuttings were located. These drill cuttings have been identified and incorporated into the GIS for sampling.

The distribution of wells selected for sampling is illustrated in Figure 5. A list of these wells is provided in Table 1.

Table 1. Wells to sample for the Devonian Shale CO₂ Sequestration project.

PERMIT	OPERATOR	WELL	FARM_NAME	COUNTY	SEC	LTR	NUM	TOTAL_	TDFM
84653	ASHLAND EXPLORATION, INC	60	FORD MOTOR COMPANY	Pike	19	M	88	6130	361SQTC
90973	BRADLEY, CHARLES R DBA BASIN ENE	1	NORDMAN, EARLENE	Magoffin	1	O	79	2390	357CBOC
91129	KINZER, J W	1003	PIKE LETCHER LAND CO	Letcher	4	I	81	3814	341OHIO
91151	EQUITABLE PRODUCTION COMPANY	KF-4448	EQUITABLE PRODUCTION CO	Floyd	25	K	83	3964	341OLNG
91182	EQUITABLE PRODUCTION COMPANY	KL4390	HOPKINS, JC & VALENTINE	Floyd	4	N	82	2358	341OLNG
91355	KINZER, J W	1052	KINZER, J W	Pike	20	M	90	5199	347HDBG
91796	PENN-VIRGINIA OIL & GAS CORP	11	KENTENIA	Harlan	7	D	73	4327	361ODVCU
92640	EQUITABLE PRODUCTION COMPANY	KL4-504695	LOWE, A HEIRS	Pike	20	N	84	3639	341OLNG
92647	ENERGY ASSOCIATES, INC	1	ASHER, IDA ET AL	Clay	8	G	72	2755	357CLNT
92715	COLUMBIA NATURAL RES, INC	24526	BUSH, JOHN ET AL	Floyd	9	L	83	3268	341OHIO
93241	EQUITABLE PRODUCTION COMPANY	505045	EVANS, E J	Knott	12	L	79	2770	341HURNL
93411	EQUITABLE PRODUCTION COMPANY	505040	EQUITABLE PRODUCTION COMPANY	Breathitt	7	M	78	2760	341OLNG
93453	EQUITABLE PRODUCTION COMPANY	504725	EQUITABLE PRODUCTION CO	Knott	11	I	78	3550	341OLNG
93520	EQUITABLE PRODUCTION COMPANY	504984	EQUITABLE PRODUCTION CO	Knott	9	J	77	3682	341OLNG
93560	EQUITABLE PRODUCTION COMPANY	504384	THE ELK HORN COAL CORP	Floyd	22	M	81	2510	341OLNG
93762	C D & G ENT - JOHNSON, GARY C	1	MCGINNIS, BASIL ET AL	Martin	19	P	83	2879	341OHIO
93844	BRADLEY, CHARLES R DBA BASIN ENE	1	RIDDLE, TROY	Perry	6	G	78	3905	341OHIO
94045	COLUMBIA NATURAL RES, INC	24875	KENTUCKY BERWIND LAND CO	Pike	14	K	87	4975	341OHIO
94086	INTERSTATE NATURAL GAS CO	4	DAVIS, IDA	Knott	24	K	81	3190	341OHIO
94088	EQUITABLE PRODUCTION COMPANY	505313	EQUITABLE PRODUCTION CO	Pike	16	K	86	4182	341OLNG
94107	EQUITABLE PRODUCTION COMPANY	505333	EQUITABLE PRODUCTION CO	Pike	14	L	86	4360	341OLNG
94174	COLUMBIA NATURAL RES, INC	23798	HAYS, LUTITIA ET AL	Knott	8	J	79	3256	341OHIO
94175	EQUITABLE PRODUCTION COMPANY	504790	TIERNEY, LAWRENCE E	Pike	19	N	86	4150	341OLNG
94210	EQUITABLE PRODUCTION COMPANY	565386	EQUITABLE PRODUCTION CO	Pike	13	J	84	4620	341OLNG
94229	COLUMBIA NATURAL RES, INC	24945	THE ELK HORN COAL CORP / HUNT	Floyd	4	L	83	3126	341OHIO

Figure 3. Chart showing nomenclature of Mississippian and Devonian shales of eastern Kentucky.

Figure 4. Initial distribution of Devonian shale drill cuttings sample sets.

Figure 5. Eastern Kentucky Devonian Shale CO2 Sequestration sample locations.

The Kentucky Well Sample and Core Library is a facility housing a legacy data set of subsurface information for the Commonwealth. Drill cuttings are received at the warehouse, cataloged, and shelved while awaiting processing. Sample bags are identified by well and depth information and roughly sorted. The contents of each bag are emptied into a 160 mesh copper sieve with a serial identifier. For each sample bag, a sample label is prepared with the sieve number, footage, and catalogue number. This label is mounted on a plastic insert that will become a permanent part of the sample collection. Once loaded into the sieves, the samples are placed on a tray and run through a conveyor driven sample washer. For this project, the drying oven is turned off and all samples are air-dried. After drying, the plastic identifying tags are matched to the sieves. The tag and cuttings are stored together in a self-sealing polyethylene bag. The identified bags are then sorted by depth and loaded into corrugated boxes for storage in the library.

For this project, the intervals to be samples are identified from the drillers' logs and geophysical logs on file (see **Figure 4** for a type log). Equal amounts of cuttings from each interval are incorporated into the composite sample for adsorption and petrographic analysis. If there are multiple sample bags for the same interval, only one bag is sampled. The composite samples are mixed and split into fractions as required for each procedure.

Unwashed drill cuttings that have been checked in and cataloged

Pallet of unwashed drill cuttings as received (not cataloged)

Drill cuttings readied for sorting and processing.

Sorting samples in preparation for loading into polyethylene sample bags.

Sorted drill cuttings are packed into individual bags

Leah Barth collecting composite sample for CO₂ adsorption and petrographic analyses

Splitting composite sample for petrographic and adsorption analyses

Cortland Eble examining samples for petrographic analysis

Well samples with completed analyses are shown in Table 2.

Table 2. Gas Storage Capacity of Completed Samples

Sample	Formation	CO₂ scf/ton	TOC
107928-1	341OHIOU	37.5	0.69
107928-2	341HURNL	67.6	2.95
107928-3	341OHIOU	34.6	1.6
121774-1	341OHIO	126.5	3.66
124789-1	341OHIOU *	740.8	3.26
124789-2	341HURNL *	2077.6	4.62
124789-3	341OHIOU	116.2	1.78

**Samples being re-analyzed*

Adsorption isotherms for these samples are presented in Appendix A. Two samples (124789-1 and 124789-2) exhibit unexpectedly high measured values for the adsorbed volume of CO₂. Additionally, the adsorption isotherms for these samples do not exhibit the expected inflection point representative of reaching a saturated monolayer of adsorbant (the Langmuir volume). At this time, the cause of these suspected anomalies is unknown; the samples are being re-processed to verify the experimental procedures and results.

Initial estimates of CO₂ sequestration capacity have been calculated using selected data. An initial estimate of the sequestration volume of the Lower Huron was compiled using areal distribution and thickness data from Dillman and Ettensohn (1980c). Using a Langmuir volume of 67.6 scf/ft³, and an average thickness of 150 feet over the area of Boyd, Breathitt, Floyd, Johnson, Knott, Lawrence, Leslie, Magoffin, Martin, Perry, and Pike Counties combined, initial calculations indicate that 91x10¹² cubic feet of CO₂ could be sequestered in the Lower Huron. At 30 percent of this theoretical saturation, approximately 1.6 billion tons of CO₂ could be sequestered. A method is needed to extend similar analyses over the area of Kentucky underlain by Devonian shale that allows for variable shale thickness and adsorption capacities.

A procedure has been developed to use geographic information systems software (GIS) to analyze the potential total volume of CO₂ sequestration for Kentucky. The method uses a cell-based approach that enables combining shale thickness and depth information in the form of continuous grids with shale density and spatially variable CO₂ adsorption capacity data. Using a one-kilometer grid, a depth to top of shale of 1,000 feet or greater, a shale thickness of 50 feet or more, and a constant adsorption capacity equal to a thickness-weighted average of 40 scf/ft³, estimated initial CO₂ sequestration capacity of the Devonian shale in Kentucky is 27.7 billion tons. An additional advantage of this method is that capacity estimates can be calculated for counties or regions. Appendix B presents a discussion of the method and an example summary by county and region of sequestration capacity. The procedure is currently under review.

Conclusion

Collecting drill cuttings for composite sampling is proceeding. Uncatalogued sample sets continue to be identified for incorporation into the project. The sampling procedures have been revised to eliminate washing in order to increase the amount of available material in the drill cuttings. Geophysical logs are being correlated to direct sampling efforts. Sample sets are being delivered to partners for analysis. We remain in contact with Columbia Natural Gas (now owned by Triana) to schedule participation in logging and sidewall coring of an eastern Kentucky well. Preliminary estimates indicate a storage capacity of 27.7 billion tons of CO₂.

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Appendix A: Summary of Adsorption Isotherms

The classic theory used to describe the Type I isotherm for microporous materials with small external surface area is based on the Langmuir equation (1916). The Type I isotherm displays a steep increase in adsorption at low relative pressures due to enhanced adsorption caused by the overlapping adsorption potentials between the walls of pores whose diameters are commensurate in size with the adsorbate molecule. The type I isotherm then flattens out into a plateau region at higher relative pressure, which is believed to be due to the completion of a monolayer of adsorbed gas. The micropore volume is then thought to be filled by only a few molecular layers of adsorbate, and further uptake is limited by the dimensions of the micropores.

The Langmuir model assumes that a state of dynamic equilibrium is established between the adsorbate vapor and the adsorbent surface and that adsorption is restricted to a single monolayer. The adsorbent surface is thought to be composed of a regular array of energetically homogeneous adsorption sites upon which an adsorbed monolayer is assumed to form. The rate of condensation is assumed to be equal to the rate of evaporation from the adsorbed monolayer at a given relative pressure and constant temperature. The Langmuir equation was developed with these assumptions and takes the following form:

$$\frac{P}{V} = \frac{1}{BV_m} + \frac{P}{V_m}$$

where P is the equilibrium pressure, V is the volume of gas adsorbed at equilibrium, V_m is the volume of adsorbate occupying the monolayer and B is an empirical constant. A plot of P/V vs relative pressure should yield a straight line whose slope will yield V_m from which the surface area may be obtained. As shown on the following figures, a best fit Langmuir isotherm and the data points have been plotted for each sample.

The Langmuir Isotherm can be written:

$$V(P) = \frac{V_L P}{P_L + P}$$

P = gas pressure

$V(P)$ = predicted amount of gas adsorbed at P

V_L = Langmuir volume parameter

P_L = Langmuir pressure parameter

The difference between the measured amount of gas adsorbed ($V(P)$) and that predicted using the Langmuir Equation ($V_i(P)$) is a measure of error and is given as:

$$Err(P) = V_i(P) - V(P)$$

This error may be positive or negative. The square of the error is always positive and is a measure of how well the calculated isotherm matches the data. This error can be calculated for each point and summed giving a measure of the overall error:

$$SSE = \sum_{i=1}^N Err_i^2$$

N = number of measured points

The goodness of fit of the isotherm is expressed by calculating the correlation coefficient between the measured points and the calculated points. The results generally yield correlations that are better than $r^2 = 0.99$, and standard errors of Langmuir volumes of $\pm 2\%$. The errors for the samples are found at the bottom of the datasheets included with each sample.

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107928-1 3600-4000 ft. Ohio Shale (upper part)

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
61	2.6
141	6.1
209	8.6
262	11.0
326	13.1
395	15.0
484	16.7
589	17.9
811	18.6

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	37.5
Pressure (PSIA)	681.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.88 Density g/cc 2.756

107928-2 4400-4600 ft. Lower Huron Member

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
47	8.9
109	19.7
172	27.6
252	35.9
315	41.2
383	45.1
469	46.8
572	48.0
803	48.7

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	67.6
Pressure (PSIA)	243.7

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.97 Density g/cc 2.660

**107928-3 4600-5000 ft. Rhinestreet and
Olentangy Members**

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
49	5.3
109	9.9
177	13.5
248	17.4
320	19.5
391	22.4
483	24.1
590	24.8
806	25.0

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	34.6
Pressure (PSIA)	253.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.98 Density g/cc 2.749

**121774-1A 3500-3720 ft. Ohio Shale
(Undifferentiated)**

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
23	2.9
50	6.4
82	9.8
103	11.8
130	14.2
185	18.9
251	24.8
321	31.3
392	37.2
512	48.4
705	68.9

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	126.5
Pressure (PSIA)	989.8

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.91 Density g/cc 2.550

RN124789 1A 2680-2990 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
26	3.1
55	6.2
76	8.3
111	12.1
133	15.4
191	22.3
259	29.6
334	37.7
402	43.2
517	54.9
595	61.6

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	740.8
Pressure (PSIA)	6419.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.49 Density g/cc 2.597

RN124789 S2A 2990-3110 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
29	3.9
45	6.7
68	10.4
94	14.0
122	17.4
176	24.4
240	34.0
309	44.4
380	54.0
496	69.8
602	96.9

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	2077.6
Pressure (PSIA)	14283.5

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.04 Density g/cc 2.579

RN124789 3A 3110-TD

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
32	4.2
49	6.0
74	8.2
110	11.4
136	13.6
193	17.9
253	23.6
326	30.4
394	35.6
512	45.7
663	60.3

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	116.2
Pressure (PSIA)	957.9

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.77 Density g/cc 2.679

Appendix B: GIS Analysis of the Distribution and Estimated CO₂ Storage Volume of the Devonian Shale in Kentucky

Note: Grid data sets are indicated in matrix notation using the courier type face, i.e.,
[grid_data]

Geographic information system (GIS) software was used to perform an analysis of the thickness and distribution of the Devonian black shale in Kentucky. The initial goal is to calculate the number of tons of shale in place by county for those areas with drilling depths to the shale of at least 1,000 feet and a shale thickness of at least 50 feet. These cutoffs were selected to ensure reservoir integrity (deeper than the expected depth of surface fracturing) and gas reservoir potential. With the number of tons of shale being determined, a series of factors to calculate the sequestration potential in tons of CO₂ are derived based on measured CO₂ storage capacity and shale density. For GIS, ESRI's ArcView 3.2 and Spatial Analyst were used. The Kentucky Geological Survey uses a server running SQL-2000 for data storage. Data are accessed with tables linked to a graphic user interface implemented using Microsoft Access 97. Access queries were composed to compile point data sets consisting of the locations and values of Devonian shale stratigraphic tops and thickness. The formation tops data were maintained as drilling depth to the top of the formation rather than elevations with respect to sea level. Open database connectivity (ODBC) services are available from ArcView. The Access query results were added to the GIS as tables using the SQL Connect facility and then converted to shape files.

```
SELECT dbo_well_identification.record_number AS recno,  
dbo_geographic_location.north_latitude AS lat,  
dbo_geographic_location.west_longitude AS lon, dbo_formation_tops.pick_fm,  
dbo_geographic_location.surface_elevation AS elev, dbo_formation_tops.fm_top,  
dbo_formation_tops.fm_base, [fm_base]-[fm_top] AS thick  
FROM ((dbo_geographic_location INNER JOIN dbo_geographic_region ON  
dbo_geographic_location.location_index = dbo_geographic_region.location_index)  
INNER JOIN dbo_well_identification ON dbo_geographic_location.location_index =  
dbo_well_identification.location_index) INNER JOIN dbo_formation_tops ON  
dbo_well_identification.record_number = dbo_formation_tops.record_number  
WHERE (((dbo_formation_tops.pick_fm)="341OHIO" Or  
(dbo_formation_tops.pick_fm)="341CHAT" Or  
(dbo_formation_tops.pick_fm)="341NALB") AND ((dbo_formation_tops.fm_top) Is  
Not Null) AND ((dbo_formation_tops.fm_base) Is Not Null) AND (([fm_base]-  
[fm_top])>0) AND ((dbo_formation_tops.type_of_top)="s") AND  
((dbo_geographic_location.ns_feet)>0) AND ((dbo_geographic_location.n_or_s) Is  
Not Null) AND ((dbo_geographic_location.ew_feet)>0) AND  
((dbo_geographic_location.e_or_w) Is Not Null) AND  
((dbo_geographic_location.carter_section)>0) AND  
((dbo_geographic_location.carter_letter)>=" A") AND  
((dbo_geographic_location.carter_number) Is Not Null));
```

Sample SQL query composed with the Access GUI for compiling Devonian shale stratigraphic and location point data.

Existing polygon shape files of the Kentucky counties, faults, and the subsurface distribution of the Devonian shale in Kentucky ([Subsurf]) were employed in the analysis. The shape file of the subsurface distribution of the shale was converted to a grid for use in the spatial analysis. Each cell of this grid contained a value of 1 (true) if the shale existed in the subsurface over the area of the cell. All other cells were set to null, the no data value. All grids were computed with 1,000-meter (1 kilometer) cell dimensions. Analyses were performed using the North American Datum of 1927 (NAD27) with the projection set to UTM zone 16.

Subsurface distribution of the Devonian shale (blue, shaded) with stratigraphic data points.

Subsurface distribution of the Devonian shale (blue, shaded) with stratigraphic data points for the Lower Huron Member of the shale.

For deriving drilling depth and thickness maps, grids were interpolated from point data using the inverse distance weighted (IDW) nearest neighbor method. The interpolated data were processed to establish which grid cells fit the selection criteria of 1,000 feet or deeper drilling depths and a shale thickness of at least 50 feet.

```

Interpolate grid, [Depth], using drilling depth from point file
Interpolate grid, [Iso], using thickness data from point file
Map Query [Depth]>=1000 = [Deep]
Map Query [Iso]>=50 = [Thick]
Calculate [Deep]*[Thick] = [Temp01]
Calculate [Temp01]*[Subsurf] = [Temp02]
([Temp02] = 0.AsGrid).SetNull([Temp02]) = [DeepThick]

```

Method for deriving a grid dataset indicating the distribution of shale at least 50 feet thick and 1,000 feet deep.

To restrict the volume calculations to the limits of the distribution of thicker and deeper shale, the [Iso] and [DeepThick] grid data sets were multiplied together to produce a new grid, [Target].

To limit the number of calculation steps required to derive volume and sequestration potential estimates, conversion factors were derived to convert the thickness (isopach in feet) data in [Target] to million tons of shale and then directly to CO₂ tons. For conversion to million tons of shale:

$$MMTons_{shale} = \frac{thickness * \frac{0.3048m}{ft} * (1000m)^2 * density * 1.102}{1000000} \quad \text{Eq. 1.}$$

where: *thickness* = thickness of shale in feet
1000 = cell size in meters
density = bulk density from compensated density log
1.102 = density conversion factor to convert from grams per cubic centimeter to tons per cubic meter

The conversion factor suggested by equation 1 varies with the density of the shale. Substituting different shale densities, the factor, CfMMTons, would be one of:

2.5 g/cc (log estimated density for Lower Huron)	= 0.840
2.6 g/cc (log estimated density for upper part of shale)	= 0.873
2.65 g/cc (log handbook typical shale density)	= 0.890

To calculate million tons of shale per cell, then:

[Target]*CfMMTons.AsGrid = [MMTons]

Different conversion factors could be derived for standard reservoir analysis. Additionally, the distribution of porosity, water or oil saturation data, and others could be gridded and used to derive oil or gas in place estimates.

A second factor is required to convert tons of shale to estimated tons of CO₂ sequestered based on the gas content from CO₂ adsorption data. Using 17.25¹ Mcf CO₂ per ton of CO₂, there will be 57.97*(gas content [scf/ton]) tons of CO₂ per million tons of shale. That is:

$$TonsCO_2 = \frac{ft_{CO_2}^3}{ton_{shale}} * 1000000 * \frac{Mcf}{1000 ft_{CO_2}^3} * \frac{ton_{CO_2}}{17.25 Mcf} = 57.97 \quad \text{Eq. 2}$$

Multiplying by the measured gas content yields a selection of factors to convert tons of shale to tons of CO₂ sequestered:

- 1739.1 tons CO₂ per million tons shale (gas content = 30 scf per ton, minimum measured gas content)
- 2318.8 tons CO₂ per million tons shale (gas content = 40 scf per ton, thickness weighted average gas content)
- 3930.4 tons CO₂ per million tons shale (gas content = 67.8 scf per ton, maximum measured gas content, Lower Huron)

For carbon sequestration potential analysis, the two derived factors can be combined to enable calculating CO₂ capacity in million tons per cell directly from thickness data. Using a gas content of 40 scf/ton, a shale density of 2.6 g/cc, and a 1000-meter cell size, the tons of CO₂ per cell is 2024.3 per foot of shale thickness, thus:

$$[Target] * (2024.3).AsGrid = [CO2Tons]$$

The values calculated for each cell require summation for specific regions to obtain totals. With the county polygon theme active, the ArcView Summarize Zones procedure (available from the Analysis menu command) was used to summarize the data by county. The field defining the zones was the county name and the [CO2Tons] grid theme was selected for summarizing. A table of summary statistics was computed that could be joined to the original county table for mapping and additional analysis.

Summary by county of potential sequestration totals (gas content 40 scf/ton, shale density 2.6 g/cc, cell size 1,000 meters):

Name	Basin	Count	Min	Max	Mean	MMTonsCO2
BELL	160	949	0.24	1.52	0.51	486.8
BOYD	160	420	1.03	1.70	1.39	583.9
BREATHITT	160	1293	0.38	1.05	0.60	775.2
CARTER	160	329	0.34	1.26	1.05	346.6
CLAY	160	1236	0.24	0.48	0.35	433.2
ELLIOTT	160	292	0.29	1.14	0.92	267.2
FLOYD	160	1040	0.27	1.79	1.42	1,474.4
GREENUP	160	339	0.99	1.38	1.24	421.7

¹ 17.25 Mcf CO₂ per ton CO₂ is the conversion factor used by the U.S. EPA. Conversion is derived from gas laws and is valid for 60°F and 1 atmosphere pressure.

HARLAN	160	1211	0.31	1.17	0.76	918.6
JACKSON	160	275	0.21	0.34	0.25	69.4
JOHNSON	160	657	0.86	1.67	1.28	839.8
KNOTT	160	918	0.78	1.42	1.06	969.9
KNOX	160	1017	0.20	0.47	0.31	318.5
LAUREL	160	1146	0.16	0.38	0.22	255.7
LAWRENCE	160	1089	0.20	1.85	1.37	1,490.6
LEE	160	232	0.22	0.50	0.35	81.6
LESLIE	160	1066	0.38	0.79	0.55	590.8
LETCHER	160	894	0.21	1.70	1.13	1,012.2
MAGOFFIN	160	793	0.63	1.20	0.92	730.8
MARTIN	160	631	1.23	2.32	1.76	1,113.1
MCCREARY	160	703	0.10	0.24	0.15	107.8
MENIFEE	160	16	0.37	0.42	0.39	6.2
MORGAN	160	710	0.25	1.19	0.70	496.8
OWSLEY	160	497	0.13	0.44	0.34	168.0
PERRY	160	892	0.37	1.04	0.71	630.4
Name	Basin	Count	Min	Max	Mean	MMTonsCO2
PIKE	160	2056	0.82	3.60	2.17	4,467.3
POWELL	160	7	0.31	0.34	0.32	2.2
ROCKCASTLE	160	4	0.19	0.21	0.20	0.8
ROWAN	160	2	0.54	0.54	0.54	1.1
WHITLEY	160	1161	0.16	0.70	0.22	261.1
WOLFE	160	525	0.20	0.81	0.45	237.1
Appalachian	160 Total					19,558.9
MARSHALL	250	29	0.39	0.56	0.48	13.9
Jackson Purchase	250 Total					13.9
EDMONSON	300	670	0.12	0.40	0.24	157.5
HARDIN	300	220	0.13	0.18	0.16	35.3
HART	300	178	0.11	0.20	0.15	26.4
MEADE	300	106	0.18	0.22	0.20	21.6
PULASKI	300	58	0.14	0.18	0.16	9.3
WARREN	300	424	0.12	0.38	0.20	84.0
Cincinnati Arch	300 Total					334.2
BRECKINRIDGE	315	1426	0.10	0.26	0.19	274.8
BUTLER	315	1130	0.11	0.41	0.28	320.3
CALDWELL	315	898	0.27	0.67	0.48	430.0
CHRISTIAN	315	1870	0.11	0.58	0.25	470.0
CRITTENDEN	315	968	0.31	0.90	0.66	634.1
DAVIESS	315	1255	0.12	0.46	0.32	404.1
GRAYSON	315	1277	0.12	0.49	0.27	343.6
HANCOCK	315	516	0.15	0.54	0.29	150.5
HENDERSON	315	1233	0.11	0.64	0.45	560.8
HOPKINS	315	1464	0.14	0.64	0.41	595.7
LIVINGSTON	315	696	0.42	0.67	0.60	415.6
LOGAN	315	966	0.12	0.25	0.19	183.1
LYON	315	620	0.28	0.59	0.46	284.8
MCLEAN	315	671	0.14	0.56	0.39	259.9
MUHLENBERG	315	1266	0.12	0.59	0.34	425.4
OHIO	315	1549	0.16	1.09	0.37	573.4
TODD	315	879	0.10	0.31	0.18	156.9
TRIGG	315	848	0.16	0.34	0.24	200.6

UNION	315	953	0.57	0.81	0.69	657.7
WEBSTER	315	878	0.17	0.68	0.51	445.1
Illinois Basin	315 Total					7,786.5
	Grand Total					27,693.5
Years sequestration available at 80,000,000 tons CO2 per year						346.2

The values shown in this table are provided to illustrate an application of the estimation method described in this appendix. The numbers are subject to revision and do not represent final conclusions of this project.