Fracture Dissolution of Carbonate Rock: An Innovative Process for Gas Storage

TOPICAL REPORT

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ABSTRACT

The goal of the project is to develop and assess the feasibility and economic viability of an innovative concept that may lead to commercialization of new gas-storage capacity near major markets. The investigation involves a new approach to developing underground gas storage in carbonate rock, which is present near major markets in many areas of the United States. Because of the lack of conventional gas storage and the projected growth in demand for storage capacity, many of these areas are likely to experience shortfalls in gas deliverability. Since depleted gas reservoirs and salt formations are nearly non-existent in many areas, alternatives to conventional methods of gas storage are required. The need for improved methods of gas storage, particularly for ways to meet peak demand, is increasing. Gas-market conditions are driving the need for higher deliverability and more flexibility in injection/withdrawal cycling. In order to meet these needs, the project involves an innovative approach to developing underground storage capacity by creating caverns in carbonate rock formations by hydraulic fracturing and acid dissolution.

The first phase of the project (Budget Period I), which is summarized in this report, involves preliminary geologic and economic analysis of this new method for creating gas storage. This information contributes to providing an initial assessment of the cost and feasibility of applying the new technology. A final and more detailed cost analysis of the method will be done in the third phase of the project.

Regional geologic analysis includes compilation of a large amount of data from the carbonate formations in six states. These states were selected based on their location near major natural-gas markets and pipelines: Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York. Based on regional stratigraphy within the project area, seven major carbonate units were recognized and studied. Geological information was compiled for each of these units and used to map their distribution. The following types of maps were constructed for each of the carbonate units: structural contour, depth to top of carbonate, thickness, occurrence of carbonate over specific depth ranges, and occurrence of limestone over specific depth ranges. Geographic Information Systems (GIS) software was used extensively for producing and integrating the maps.

To analyze the requirements for creating storage volume, the following aspects of the dissolution process were examined: weight and volume of rock to be dissolved; gas storage pressure, temperature, and volume at depth; rock solubility; and acid costs. Hydrochloric acid was determined to be the best acid to use because of low cost, high acid solubility, fast reaction rates with carbonate rock, and highly soluble products (calcium chloride) that allow for the easy removal of calcium waste from the well. Despite the organic acids offering certain advantages over the inorganic acids, the cost of using any of the organic acids is prohibitive.

A process design was developed for the dissolution process that incorporates proven technologies for drilling wells, storing and pumping inorganic acids, and treating the aqueous waste streams exiting the underground storage cavern. The waste treatment design incorporates a constructed wetland treatment system that will drastically reduce the levels of green house gases (carbon dioxide) emitted from the dissolution of carbonate rock. A preliminary economic analysis of this design considered capital costs, well-design options and costs, waste treatment options, and comparison with other gas storage costs. The optimum rock type and properties were identified from an analysis of the gross-earnings costs, which varied significantly with depth. Results of this analysis show that the fracture-acid dissolution method is competitive with

other means for creating underground gas storage. Design considerations and economic calculations indicate that the new fracturing and dissolution method will be applied most advantageously to carbonate formations deeper than 4000 feet, with limestone at depths between 6000 and 9000 feet preferred. In order to identify areas that are potentially suitable for applying the new technology to creating storage volume, a series of maps was produced using carbonate depth and thickness criteria. Large areas of West Virginia, Pennsylvania, and New York are identified as potentially suitable for developing gas storage in carbonate rock by using the new fracturing and acid-dissolution technology. Smaller areas are identified in Indiana, Ohio, and Kentucky. Before applying the technology in any of these areas, specific geologic properties should be examined in greater detail than was done in the regional analysis.

The next phase of the investigation will include detailed analysis and modeling of the processes involved in creating storage capacity, including induced fracturing and acid dissolution of the rock. Specific areas, based on the regional analysis completed, will be selected for more detailed geologic characterization of the properties relevant to applying the new technology. The third and final phase of the investigation will include modeling field performance, preparing a final design, and performing an economic analysis. The purpose of the final design is to facilitate full-scale deployment of the new technology. Demonstration of the commercialization potential of gas storage in carbonate rocks will open up new geographic areas for developing storage capacity. The technology is expected to have general application to many geographic areas because of the widespread occurrence of carbonate formations.

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INTRODUCTION

Currently, natural gas is in high demand in many regions of the United States, especially the Northeast. Hence, there is an increasing effort focused on developing new methodologies that will make natural gas more readily available, which should ultimately reduce the cost of natural gas to consumers. Of particular interest are more efficient and safe means for storing large quantities of natural gas close to major pipelines or high usage areas. The primary focus of this project is to evaluate the feasibility of creating underground natural gas storage capacity in optimal locations via the acid dissolution of carbonate rock formations. The analysis includes compilation of a large amount of data from carbonate formations in six states (Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York), which were selected in consultation with DOE based on location near major natural-gas markets and pipelines.

The basic concept of the fracture and acid-dissolution method is to drill to depth, fracture the carbonate rock layer, and then create a cavern using an aqueous acid to dissolve the carbonate rock. Following waste fluid removal, the resulting cavity can be used as a subsurface natural gas storage reservoir. Abundant carbonate rock formations worldwide make the project worthwhile for the entrepreneur and consumer alike, especially when the facility is to be located near large gas markets where current gas storage capacity is insufficient to meet demand. An additional benefit of the fracturing and acid-dissolution method is its suitability for developing storage capacity of specific volume near industrial facilities or power-generating plants.

Specifically, the first phase of this project has focused on developing guidelines and a cost estimate for developing gas storage facilities in carbonate rock formations that have negligible innate gas storage capacity (i.e., low permeability and/or porosity). There are two primary factors that determine the viability of creating an underground natural gas storage reservoir via acid dissolution of carbonate rock: the existence of carbonate rock formations at the appropriate location and depth (geology) and the cost associated with dissolving large quantities of limestone with aqueous acids (dissolution economics).

RESULTS AND DISCUSSION

Subsurface Characteristics of Existing Storage and Producing Fields (Task 1)

The goal of this part of the project (Task 1) was to use existing databases to identify the range of geologic and reservoir properties of producing gas formations and existing underground gas storage fields in carbonate formations.

Using the major gas atlases (Kosters et al., 1989; Bebout et al., 1993; Robertson et al., 1993; Roen and Walker, 1996) and a recent publication of the American Gas Association (2002), values for basic geologic and reservoir properties for producing carbonate reservoirs were compiled (Table 1). Additionally, the GASIS Release 2 data (Energy & Environmental Analysis, Inc., 1999) was searched, but was found not to be applicable with respect to identifying the reservoir properties.

Various data sources were investigated for identifying the geologic and reservoir properties of existing carbonate formations used for gas storage. A thorough literature search was conducted and enquiries were made at state geological surveys in the six state study area (Indiana, Kentucky, New York, Ohio, Pennsylvania, and West Virginia). One of the major impediments to finding this type of data is that there are few carbonate formations being exploited for gas storage compared to sandstone formations (American Gas Association, 2002), as sandstone formations generally have higher permeability, which is more favorable for traditional gas storage in aquifers and depleted reservoirs. Most of the data found for gas storage reservoirs in carbonate rocks are from Buschbach and Bond (1974).

The data compiled in Tables 1 and 2 apply to permeable formations used for traditional gas storage. Although they do not apply directly to development of gas storage by the fracturing and acid-dissolution method, they provide a basis for comparison with existing fields. For example, high permeability of the carbonate formation is a potentially undesirable property for creation of cavern storage by acid dissolution due to the possibility of leakage. Although initial permeability is not desirable, the presence of porosity is beneficial in contributing to the storage capacity. The presence of at least a small amount of porosity can be helpful in initiating induced fracturing. Induced fractures will be contained by using the proper fracturing technology (to be studied in the next phase of the project during Budget Period II) and by the presence of overlying non-carbonate rock. Natural fractures in the rock are not desirable because of the possibility of leakage. In summary, criteria for selecting suitable carbonate rocks for the fracturing and acid-dissolution method are: low permeability, at least a small amount of porosity, and minimal natural fracturing.

A large amount of regional information was compiled for the carbonate formations of Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York. This information is discussed in the section of this report on “Regional Survey of Carbonate Formations”.

Table 1. Summary of geologic and reservoir properties for producing carbonate reservoirs in four major areas of the United States. Data compiled from Kosters et al. (1989), Bebout et al. (1993), Robertson et al. (1993), Roen and Walker (1996), and a recent publication of the American Gas Association (2002). Perm=permeability; Ave= average; #obs=number of data values; nd = no data available

	Rocky Mountain			**Texas**			**Mid Continent**			**Appalachian**		
	ave	range	#obs	ave	range	#obs	ave	range	#obs	ave	range	#obs
Porosity (%)	8.1	2 - 25	160	9.95	1.0-21.0	243	10.9	2.0-22.0	52	10	2-23	192
Perm (md)	29.4	0.01-500	92	34.4	0.01-400	201	95.3	1.0-1740.0	27	13	0.1-57	13
Depth (ft)	8085	1106-18K	186	9596	1100-24K	334	7220	1744-24K	82	2212	162-7K	340

Table 2. Summary of geologic and reservoir properties for gas storage in carbonate rocks. reservoirs in four major areas of the United States. Data compiled from Buschbach and Bond (1974) and American Gas Association (2002).

	Range	**Average**	**# Observations**
Porosity (%)	8.9 - 17.5	13.5	9
Perm (md)	18 - 649	235	6
Depth (ft)	14 - 693	264	9
Thickness (ft)	670 - 3050	1470	10

Requirements for Creating Storage Volume (Task 2)

Acid Dissolution of Carbonate Rock

In order to dissolve large deposits of limestone using aqueous acids, two reaction fundamentals need to be considered: kinetics and equilibria. The reaction kinetics determine the rate at which dissolution can occur, and reaction equilibria combined with product solubility determine the theoretical yield and maximum concentration of species exiting from the dissolution process. Obviously, one would prefer that the dissolution reaction rate be fast and the reaction equilibria favor the formation of highly soluble salt products. Due to the common nature of the reagents involved in the dissolution process, much of the reaction kinetics, reaction equilibria, and reactant/product solubility data have already been measured and are readily available in the open literature.

Limestone deposits can be dissolved in aqueous media using an appropriate acid via the reaction mechanism shown below.

$$\mathrm{HX(aq)} + \mathrm{CaCO_3(s)} \leftrightarrow \mathrm{CaX_2(aq)} + \mathrm{H_2CO_3(aq)} \leftrightarrow \mathrm{CaX_2(aq)} + \mathrm{CO_2(g)}$$

There are several important considerations that must be taken into account before the optimal acid can be selected. These parameters include:

1) acid cost and availability;
2) aqueous solubility of resulting calcium salts;
3) acid and/or salt toxicity;
4) waste remediation considerations;
5) corrosion characteristics;
6) the need for combustion and/or evaporation controls (for organic acids);
7) dissolution reaction rate;
8) dissolution reaction equilibrium constant;
9) pKa for acid dissociation in water; and
10) prior use in related oil and gas applications.

Criteria 1, 2, 4, and 8 above were the primary factors used to identify organic and inorganic acids that may prove economically and chemically viable for the dissolution process. Though the other criteria were also considered, they had less of an impact on the overall viability of the dissolution process. A more detailed discussion of some key acid properties is provided below and in Appendix A. Discussion of the waste remediation options is included in the next section ("Process Design and Economics") of the report.

Acid Costs

Current bulk scale sale prices were obtained for several candidate acids and are shown below in Table 3. These prices are for materials to be delivered in the northeastern US and are for technical grade purity acids, with the exception of phosphoric acid (farm grade listed). Further significant reductions in acid cost could be realized following negotiations with acid producers and distributors. This is especially true given the quantity of acid to be purchased and the fact that high purity acids are not required for the dissolution process. The acid prices and purities, shown below, were also used to calculate the cost for dissolving one pound of limestone. These limestone dissolution costs provide a direct means for comparing the economic viability of the various acids. On a cost basis alone, any of the common inorganic acids appear to be a reasonable choice for the dissolution process, while the cost of most of the organic acids is prohibitive.

Table 3. Acid Cost (Chemical Market Reporter, Dec. 2003). Acids with acceptable cost are shaded.

Acid	Current Sale Price $ US / ton (wt % acid)	Acid Cost per Pound of Limestone Dissolved, $ US
*ortho*phosphoric acid (H_3PO_4)	2.7 (52%, farm grade)	0.005
sulfuric acid (H_2SO_4)	25 (100%)	0.012
hydrochloric (HCl)	68 (22 °Be, 34%)[a]	0.075
nitric acid (HNO_3)	215 (40 °Be, 68%)[a]	0.199
formic acid (HCOOH)	451 (85%)	0.244
acetic acid (CH_3COOH)	910 (95%)	0.575
3-hydroxypropionic acid ($C_3H_6O_3$)	1100 (95%)[b]	0.918
citric acid ($C_6H_8O_7$)	940 (98%)	0.921
hydrobromic acid (HBr)	1120 (48%)	1.886

[a] Note that degrees Baume or °Be is a measure of specific gravity originally based on assigning 10% NaCl solution a value of 10. In the USA, the specific gravity (i.e., purity) at 60 °F for a fluid denser than water can be expressed as sp.gr. = 145/(145-Baume).

[b] Projected sales price in 2006 (Cargill).

Reaction Equilibrium Constants

Reaction equilibria (for the carbonate dissolution reaction shown previously) determine the thermodynamic limit to which reactants can be converted into products and can be calculated using the Gibbs free energy of formation for the reagents and products. Given the elevated pressure at lower depths, it can be assumed that CO_2 would remain in solution until the salt products were pumped to the surface. Additionally, the change in enthalpy (heat generation) with reaction can be calculated from similar pure components properties. These data and the relevant equations relating them are shown below in Table 4. These calculations revealed that the equilibrium reaction constant is high (favorable) for all of the listed acids except for acetic. Further, all of the dissolution reactions are exothermic; thus, localized heating effects could increase the rate of limestone dissolution.

Calculation of Gibbs free energy of reaction from Gibbs free energy of formation values:

$$\Delta G^{o}_{rxn} = \sum_{\text{products}} \beta_j G^{o}_{f,j} - \sum_{\text{reac tan ts}} \alpha_i G^{o}_{f,i}$$

Calculation of reaction equilibrium constants (K_{eq}) from Gibbs free energy of reaction data:

$$-\Delta G^{o}_{rxn} = RT \ln K_{eq}$$

Relationship between reagent concentrations and the reaction equilibrium constant:

$$K_{eq} = \frac{\prod_j C^{\beta}_{product,j}}{\prod_i C^{\alpha}_{reactant,i}}$$

Table 4. Gibbs free energy of reaction, enthalpy change with reaction, and equilibrium constant for several limestone and dolomite acid dissolution reactions and a possible acid regeneration reaction. The favorable reactions are shaded.

Reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	$^{298}K_{eq}$
$MgCa(CO_3)_2$ (s) + 4HCl (aq) ↔ $MgCl_2$(aq) + CaCl2(aq) + $2H_2CO_3$ (aq)	-90.9	-82.6	$8.48 \cdot 10^{15}$
$CaCO_3$ (s) + H_2SO_4 (aq) ↔ $CaSO_4$ (s) + H_2CO_3 (aq)	-58.8	-8.7	$2.02 \cdot 10^{10}$
$CaCO_3$ (s) + 2HCl (aq) ↔ $CaCl_2$(aq) + H_2CO_3 (aq)	-47.9	-35.5	$2.46 \cdot 10^{8}$
$CaCO_3$ (s) + $2HNO_3$(aq) ↔ $Ca(NO_3)_2$(aq) + H_2CO_3 (aq)	-47.8	-104.	$2.45 \cdot 10^{8}$
$CaCO_3$ (s) + $2CH_3COOH$ ↔ $Ca(CH_3COO)$ (aq) + H_2CO_3 (aq)	-6.79	-38.6	15.5

Dissolution Product Solubility

The aqueous solubility of the resulting carbonate salt is also a key factor in determining the ideal acid for dissolving limestone. A low calcium salt solubility would require much greater quantities of water (and acid) to be pumped through the underground formation in order to prevent the salt product from precipitating out of solution. Aqueous solubility data for selected acids are shown in Table 5 below. The solubility data show that most of the monoprotic inorganic acids (e.g., hydrochloric, hydrobromic, nitric) yield calcium salts with high aqueous solubility, with the exception of *ortho*phosphoric acid. In contrast, the calcium salts of the diprotic (e.g., sulfuric acid) and triprotic (e.g., citric acid) acids have a very low solubility in water. Finally, the monoprotic organic acids react to form calcium salts that have moderate (e.g., calcium acetate, calcium formate) to high (e.g., calcium hydroxypropionate) solubility in water. In fact, the aqueous solubility of calcium hydroxypropionate is higher than that observed for calcium chloride. In summary, the solubility of the calcium salts derived from reactions involving sulfuric, *ortho*phosphoric, and citric acid are too low to yield a viable dissolution process. Thus, on the basis of calcium salt solubility alone, any acid yielding a calcium salt with aqueous solubility greater than 100 g/l is acceptable though higher solubility is preferred.

Table 5. Solubility of some common calcium salts in water at STP. Acids yielding reaction products having acceptable solubility are shaded.

Acid	Calcium Salt	Solubility of Calcium Salts in Cold Water (g/l)
hydrobromic acid (HBr)	calcium bromide ($CaBr_2$)	1420
nitric acid (HNO_3)	calcium nitrate ($Ca (NO_3)_2$)	1212
3-hydroxypropionic acid ($C_3H_6O_3$)	calcium hydroxypropionate ($Ca(C_3H_6O_3)_2$)	1000
hydrochloric (HCl)	calcium chloride ($CaCl_2$)	745
acetic acid (CH_3COOH)	calcium acetate ($Ca(C_2H_3O_2)_2$)	374
formic acid (HCOOH)	calcium formate ($Ca(CHO_2)_2$)	162
*ortho*phosphoric acid (H_3PO_4)	calcium *ortho*phosphate ($Ca(H_2PO_4)_2{\cdot}H_2O$)	18
sulfuric acid (H_2SO_4)	calcium sulfate (anhydrite, $CaSO_4$)	2
citric acid ($C_6H_8O_7$)	calcium citrate ($Ca_3(C_6H_5O_7)_2{\cdot}4H_2O$)	1

Selection of the Optimal Dissolution Acid

Several acids have been considered for the dissolution process (see lists in Tables 2-5), many of which have existing use in oil and gas operations, such as hydrochloric acid. Some of the advantages in using hydrochloric acid include: low cost, high acid solubility, fast reaction rates with carbonate rock, and highly soluble products (calcium chloride) that allow for the easy removal of calcium waste from the well. Furthermore, the high production of hydrochloric acid in the United States (approximately 4 million metric tons per year) is advantageous given the large quantities of acid needed to generate the proposed storage volumes. However, hydrochloric acid is corrosive to drilling equipment and the resulting waste products require greater post removal processing. Other acids that have been used previously for limestone dissolution include acetic and formic acid. Both of these organic acids are highly miscible with water, have low viscosities, are more environmentally friendly, and less corrosive to equipment. However, there are disadvantages to using acetic and formic acid: moderate reaction rates with carbonates (due to the low pKa of the acids in water), slightly less soluble calcium salt products, and moderately high acid costs. A relatively new organic acid is also worth considering, 3-hydroxypropionic acid. This organic acid is produced from corn via fermentation, easily biodegrades, and yields calcium salts that are highly soluble in water (greater solubility than calcium chloride); however, the cost of this acid is currently too high to be considered for this type of acid dissolution project. Despite the organic acids offering certain advantages over the inorganic acids, the cost of using any of these materials is prohibitive. Thus, at this time *hydrochloric acid is the most suitable for the dissolution process*.

Prediction of Gas Storage Pressure, Temperature and Volume at Depth

Forecasting reservoir conditions is critical in determining the physical properties of the natural gas contained in storage as well as the cost for generating the storage facility via acid dissolution. The key parameters needed to evaluate gas properties at depth are temperature and pressure. For all of these calculations a range of gas storage capacities were investigated, 0.25 billion cubic feet (BCF) to 2.0 BCF of natural gas at atmospheric conditions (STP, standard temperature and pressure). Additionally, the depths investigated ranged from 500 ft to 12,000 ft, which are common depths to find carbonate rock formations in the study area. In determining reservoir pressure and temperature a geophysical gradient was assumed. These gradients are accurate in areas of low tectonic activity and little underground stress, which is to be expected for the study area. A typical pressure gradient of 0.433 psi/ft was used for the hydrostatic pressure, and the pressure gradient needed to cause rock fracture was estimated to be 0.64 psi/ft. This value of 0.64 psi/ft is very conservative, as fracture gradients can exceed 1.0 psi/ft in many areas, which would allow for a greater volume of gas to be stored within a given cavity volume. Also, the fracture pressure gradient is not always linear and can vary locally depending on the geological conditions such as rock composition and stress (Zoback and Healy, 1984; Fjær et al., 1992; Rocha and Bourgoyne, 1996). For all storage calculations, it was assumed that the storage cavern could be pressurized to a value greater than the hydrostatic pressure at depth but less than the pressure needed to cause rock fracture (Figure 1); thus, a pressure gradient of 0.55 psi/ft was selected for the storage facility. Similar geothermal gradients (often linear) exist in the US and range from a 20 to 30 °C temperature increase per kilometer. For this project, a geothermal gradient of 20 °C per kilometers and a surface temperature (actually 3 m deep) of 11 °C were used to predict reservoir temperature (Lillie, 1999, Eckstein and Mauruth, 1999). Though not accounted for, a slightly lower temperature could exist because of the thick sedimentary strata found in the study area. Using these geophysical gradients reservoir conditions can be established. For instance, an 8000 ft deep storage facility can be predicted to have a pressure of 4415 psi and a temperature of 140 °F. Using these conditions, one may predict the physical behavior of the natural gas in containment and calculate the necessary cavity volume.

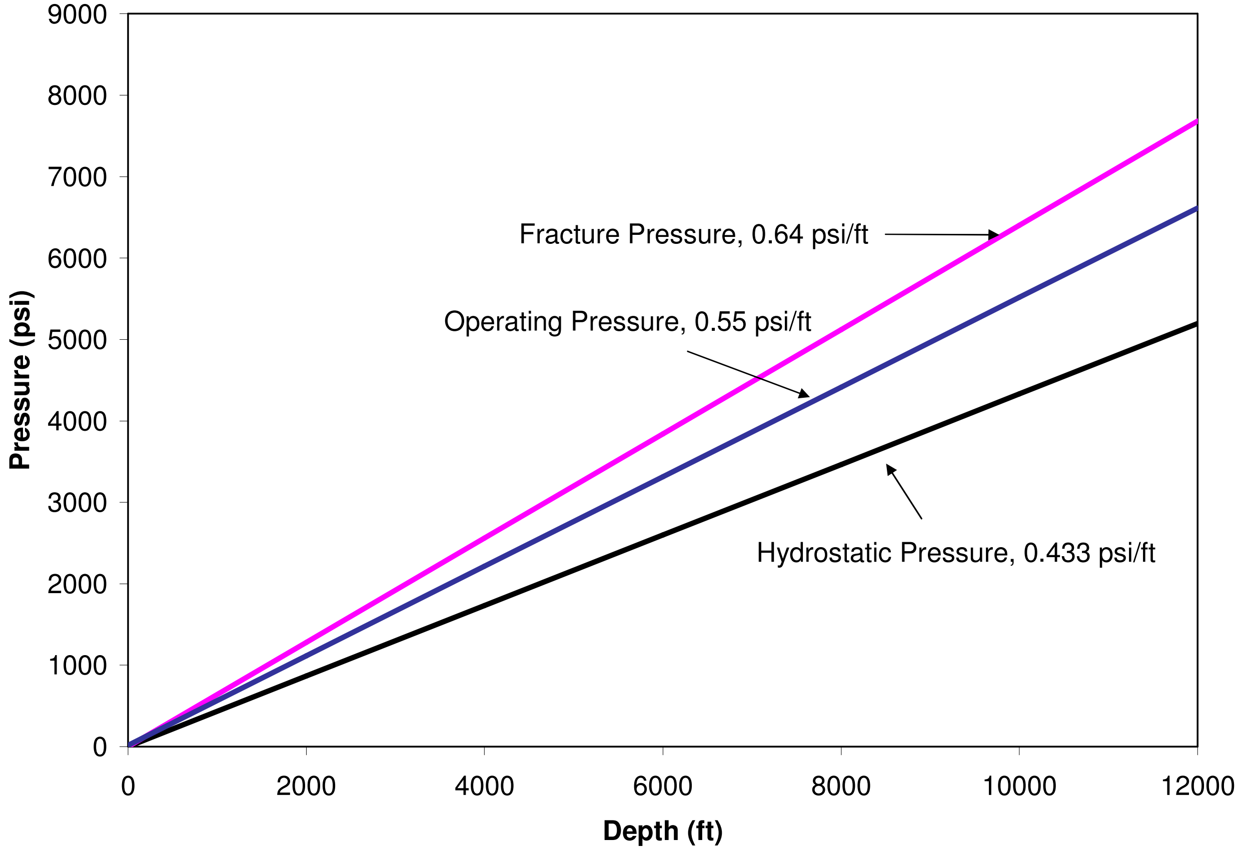


Figure 1. Estimation of hydrostatic and fracture pressures at depth. Operating pressure for gas storage facility at depth.

Natural gas is a highly compressible mixture whose density varies significantly with changes in temperature and pressure and to a lesser extent with composition. It is preferable to use experimentally measured data for natural gas density over values predicted by ideal gas law or more complicated equations of state (e.g., Peng-Robinson, SRK). The original measurements for natural gas density were reported in several journal articles, but the collected data are presented in several reference sources, including the *Handbook of Natural Gas Engineering*. Experimental gas density data (Standing and Katz, 1942) are shown in Figure 2. These data clearly illustrate that the average molecular weight of the gas, i.e., the composition, will affect the mixture density, especially at elevated pressures. The natural gas composition used for all calculations was 90 % methane and 10 % ethane, which yielded an average gas molecular weight of 17.3 g/mol, which corresponds to a 0.6 gravity gas (i.e., the specific gravity of the gas is 40% less than that of air at STP conditions).

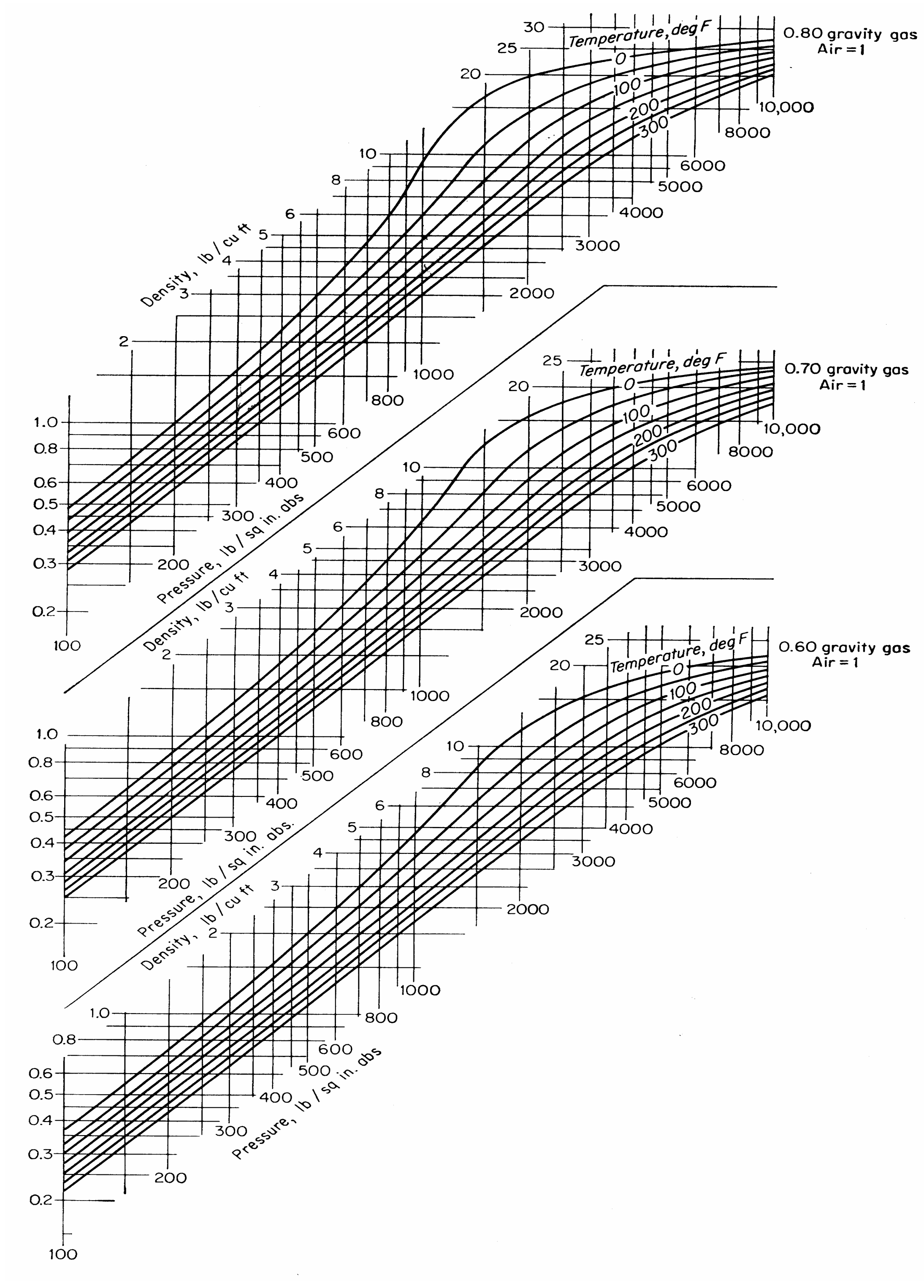


Figure 2. Density of natural gases (Standing and Katz, 1942).

The cavity storage volume required for a given quantity of natural gas is easily calculated using the gas density at STP and storage conditions.

$$\frac{V\left(\mathrm{STP}, \mathrm{ft}^3\right)}{\rho\left(\mathrm{STP}, \mathrm{lb}/\mathrm{ft}^3\right)} = \frac{V\left(\mathrm{storage\,T\,and\,P}, \mathrm{ft}^3\right)}{\rho\left(\mathrm{storage\,T\,and\,P}, \mathrm{lb}/\mathrm{ft}^3\right)}$$

The volume of underground gas volume needed at a specified depth for a given quantity of natural gas is shown in Figure 3 below.

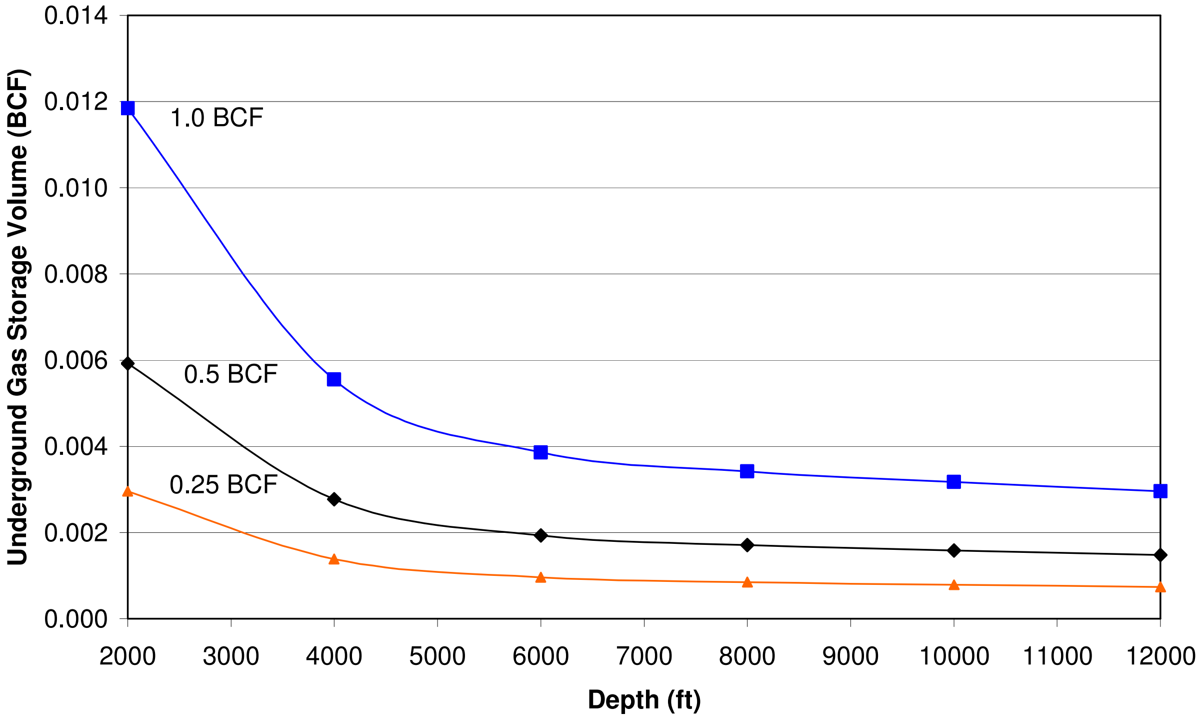


Figure 3. Variations in required underground gas storage volume with depth for 0.25 to 1 BCF (STP or zero depth conditions) of total gas storage. The plotted relationship depends heavily on previously discussed pressure and temperature gradient assumptions.

As illustrated in Figure 3, the high compressibility of natural gas makes it advantageous to develop a storage cavern at depths greater than 4000 ft, with optimal depth below 6000 ft. Below this depth the increase is gas density with depth is greatly reduced. Additionally, advantages gained by the increased gas density at depths below 6000 ft may be offset by higher drilling and operating costs.

Weight and Volume of Rock to be Dissolved

The volume of rock needing to be dissolved using aqueous acids is a function of the volume of gas to be stored in the reservoir (at STP conditions), gas density at depth, and the porosity of the carbonate rock formation:

$$V_{\text{Dissolved Rock}}\left(\text{ft}^3\right)=\left[\frac{V_{\text{gas}}\left(\text{STP},\text{ft}^3\right)\cdot\rho_{\text{gas}}\left(\text{storage T and P},\text{lb}/\text{ft}^3\right)}{\rho_{\text{gas}}\left(\text{STP},\text{lb}/\text{ft}^3\right)}\right]\left(1-\frac{\%\text{Rock Porosity}}{100}\right)$$

The mass of rock that must be removed for a given storage capacity is simply the volume of rock (accounting for rock porosity) multiplied by the density of the rock (limestone or dolomite). Using a calcium carbonate density of approximately 170 lb/ft^3, Figure 4 illustrates how the mass of rock to be dissolved varies with depth, rock porosity, and total gas storage volume.

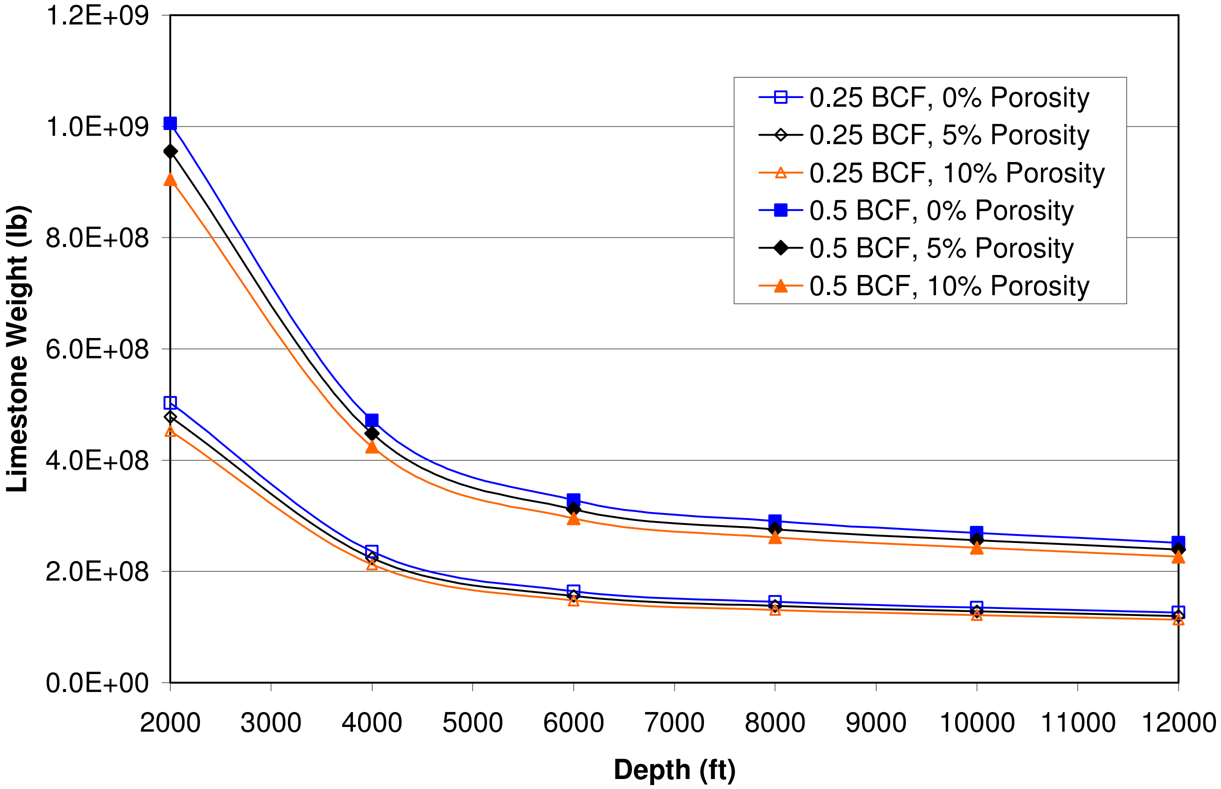


Figure 4. Weight of limestone to be removed via acid dissolution for gas storage volume of 0.25 and 0.5 BCF and limestone porosities between 0 and 10 %.

Process Design and Economics (Task 3)

The new limestone dissolution process, shown in Figure 5, involves hydrochloric acid being pumped into a fractured limestone formation, where it will rapidly react and effectively dissolve the limestone deposit. The products of this reaction, calcium chloride and carbonic acid, are highly soluble in water and will be removed via a second well, leaving behind a gas storage cavity capable of high rates of gas deliverability. Some of the key components of the process are: 1) an acid collection and storage facility, 2) an acid pumping station, 3) a clarifier for evaporating water and collecting crude $CaCl_2$ product, 4) a wetlands waste treatment facility, and 5) a $CaCl_2$ packaging facility (not shown).

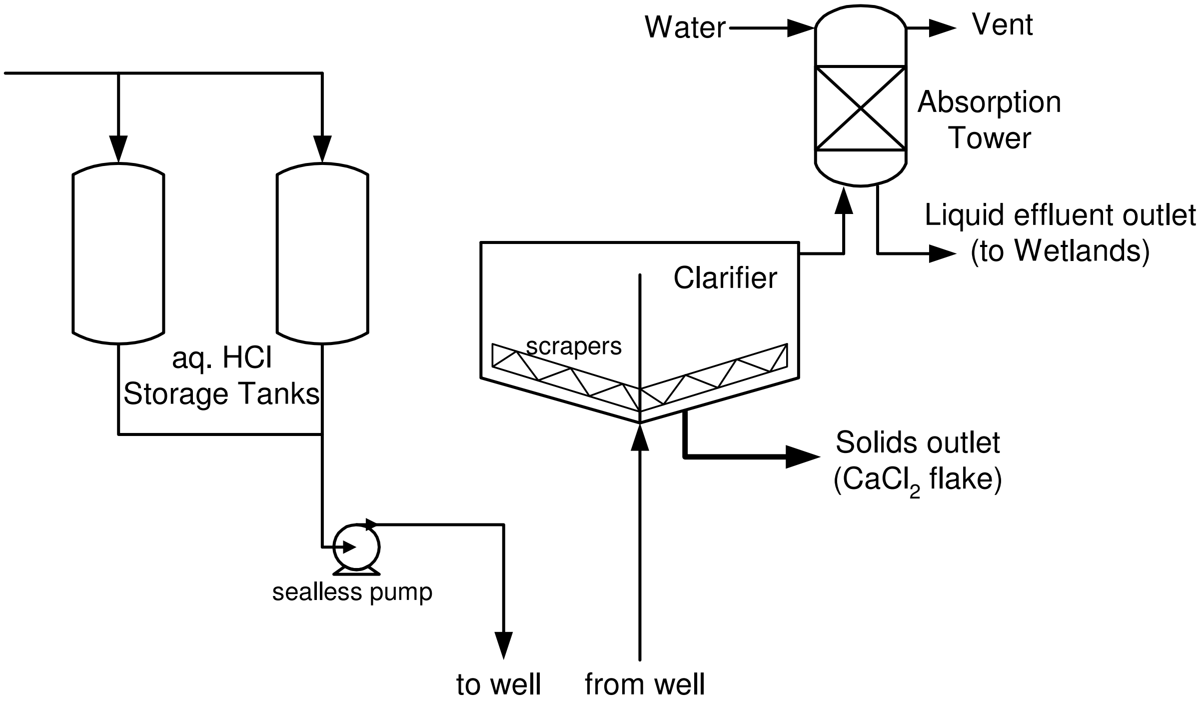


Figure 5. Simplified process flow diagram for the acid dissolution process.

Well Design Options and Costs

There exist several options for the number and placement of wells for the acid dissolution process for creating gas storage in carbonate rock. A single concentric tube design is possible and would likely yield a spherically or elliptically shaped gas storage cavern (Figure 6A). With this design, fresh acid would be pumped down the well between the inner and outer casing, similar to how salt caverns are created. Soluble salt products would be removed from the well using the smaller casing. However, there are also two-well and multi-well designs that could be used to rapidly produce an underground gas storage cavern. For the two-well designs (two-well with vertical fracture and two-well dogbone design), one well would be used to pump down fresh acid, while the other well would be used to remove spent acid products (Figure 6B). These two-well designs differ in how a water flow channel is developed between the two wells. In one case, the limestone rock is fractured (vertical fractures below 2000 ft), while in the other case a horizontally drilled hole connects the two wells. A description of the two-well designs is listed below. For cost estimation purposes, a vertically fractured two-well design cavern was selected and the cost for this type of well is listed in Table 6 for a range of depths.

Two-well with Vertical Fracture:

Description: Drill two wells and fracture vertically to connect the wells.

Method: Drill the first well, log, perform microfracture and injection tests, drill the second well, and fracture the rock between the two wells.

Restrictions/Comments: At least 2% initial porosity is needed to fracture the rock

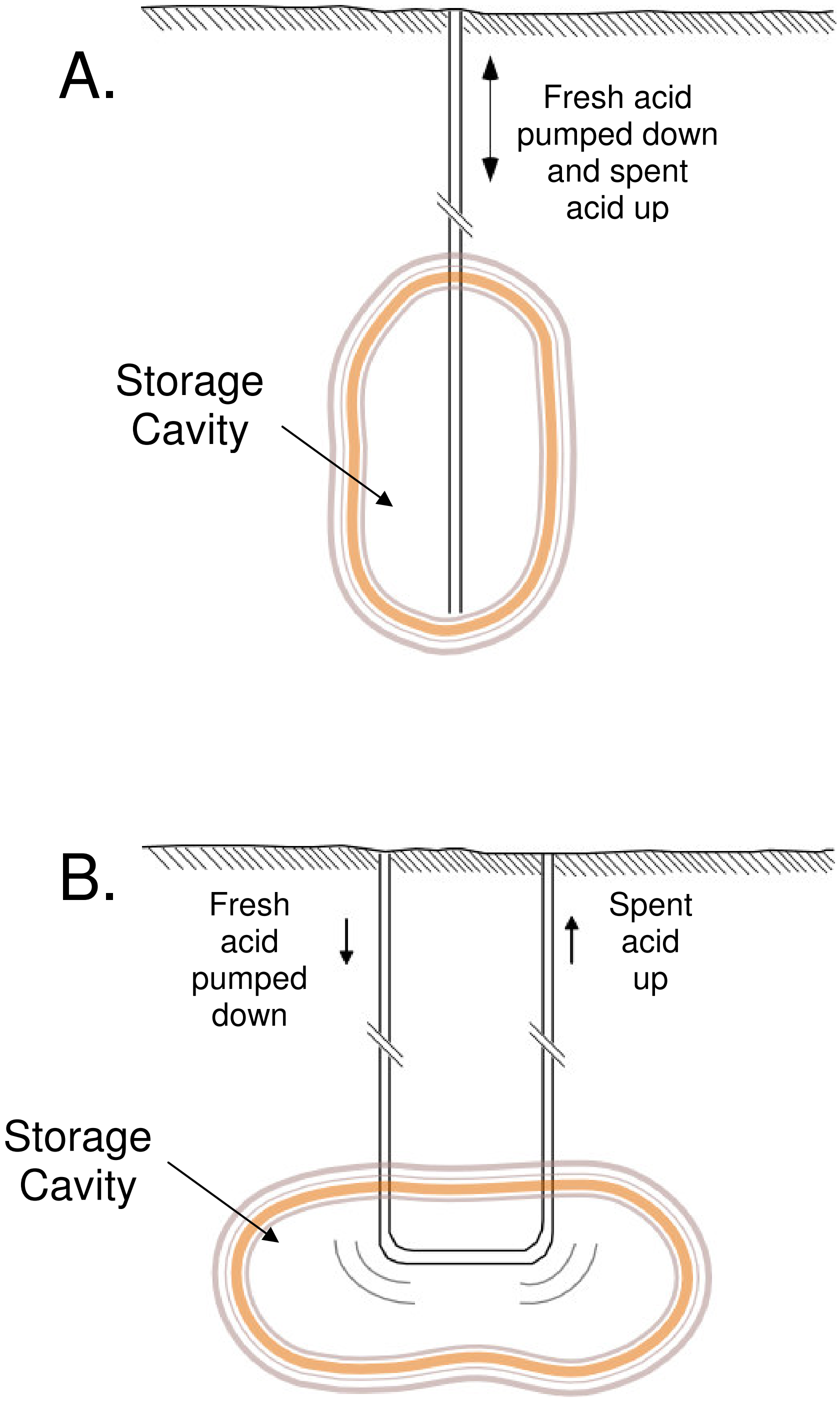


Figure 6. Well designs for creating gas-storage cavity by acid dissolution of carbonate rock. A) Single-well design; B) Two-well dogbone design.

Two-well Dogbone Design

Description: Two vertical wells with a horizontal connector.

Method: Drill the first well, log, drill the second well, and finally drill the horizontal connector between wells.

Restrictions/Comments: Most dissolution will probably occur at the corners. Distance between wells will depend on storage capacity. No initial porosity is needed.

Table 6. Approximate drilling and fracturing costs in the Northeastern US area (Source DB).

Total Depth (ft)	Completed Well[a]	Construction Well[b]	Additional Completed Costs		
			Horizontal Connection[c]	Acid Fracturing[d]	Hydraulic Fracturing[e]
4,000	\$250,000	\$150,000	\$50,000	\$20,000	\$30,000
8,000	\$1,000,000	\$500,000	\$100,000	\$100,000	\$75,000
12,000	\$2,500,000	\$1,000,000	\$150,000	\$150,000	\$200,000

a Completed injection/withdrawal storage well, 7 inch, high deliverability flow string to bottom.
b Additional slim hole well to assist in cavity building. Flow string set at total depth.
c Directionally drilled connection between wells at total depth.
d Five thousand gallon gelled acid breakdown to initiate cavity building process.
e Hydraulic fracture with proppant to initiate/accelerate cavity building process.

Waste Treatment and Green House Gas Emissions

The limestone dissolution reaction with aqueous hydrochloric acid yields calcium chloride and carbonic acid as products. These products are highly soluble in water and can be easily removed from the underground storage cavity. Upon exiting the well, these dissolution products are to be treated using two above ground process elements: a clarifier and a constructed wetland treatment system. The initial liquid/slurry will be sent to an enclosed cylindrical clarifier equipped with scrapers, where water can evaporate and solid calcium chloride product can be isolated. The calcium chloride will be sold in both liquid and solid form for road deicing purposes in the northern US, where it is the preferred deicing agent for roads ($CaCl_2$ is effective as a deicing agent at temperatures as low -15 °C). The sale of this product stream will also enhance the profitability for the dissolution project by offsetting the cost for hydrochloric acid. The secondary treatment facility consists of a newly formed wetlands area that will cover between 5 and 10 acres (depending on the size of the gas storage cavern to be developed). The plants located in this wetlands area can readily absorb dissolved carbonate anions and convert them into biomass, which can then be used to produce biodiesel fuel or be incorporated into animal feed. Since large quantities of dissolved carbon dioxide will be generated by this process (e.g., the formation of 1 BCF of gas storage at 4000 ft would produce 234 thousand tons of carbon dioxide - approximately 6% of what a typical coal power plant releases annually), this wetlands treatment system will greatly contribute to the reduction of green house gas emissions from the process. The plants in this wetlands area are also resilient to moderate levels of salts, such as calcium chloride, and have proven to be highly effective in applications involving the treatment of aqueous waste streams from power plant boilers and scrubbing towers. Thus, the waste treatment options described will greatly reduce the emissions of green house gases (carbon dioxide) and provide a revenue source that is derived from the calcium chloride product from the dissolution process.

Although other options for treating the wastewater are possible, a constructed wetland treatment system provides important economic and environmental benefits. Principles of natural wetlands will be applied to constructing a treatment system designed to ensure the desired reactions at predictable rates. This is a proven approach and has been used successfully for the treatment of various waste fluids, including refinery effluent and brines produced from oilfields (e.g., Moshiri, 1993; Hawkins et al., 1997; Gillespie et al., 2000; Huddleston et al., 2000; Moore et al., 2001, Murray-Gulde, 2003).

Fixed Capital Cost Estimation

Fixed capital costs, including both direct and indirect costs, were estimated for a limestone dissolution process that would use hydrochloric acid to create a 0.5 to 1 BCF gas storage reservoir. The various costs were calculated using Lang factors (see Table 7), which relate the costs of construction to total purchased equipment costs. The Lang factors used for this report were obtained from the process design text by Peters and Timmerhaus (1991) and are specifically for processes built in the US that require both liquids and solids handling. For this cost estimate, *delivered* equipment costs were used to estimate fixed capital costs, and these values are shown in Table 8. The key equipment items include corrosion resistant pumps, hydrochloric acid holding tanks (20,000 gal tanks), a clarifier for isolating calcium chloride products, and a wetlands wastewater treatment area for carbonic acid removal. Since these economic calculations are for only a moderately well defined process, the contingency factor (36) is higher than would be used for a process where a detailed piping and instrumentation diagram had been developed. These calculations yield a fixed capital cost of $3,270,529 US**.**

Chemical Pricing

The purchase cost of hydrochloric acid and the fair market value of the calcium chloride products was derived from up-to-date pricing information in *Chemical Market Reporter*, which provides industry average pricing for most commodity chemicals. In order to reemphasize the need for developing gas storage at depths greater than 4000 ft, variations in the total cost of hydrochloric acid as a function of storage depth are shown in Figure 7. It should be noted that the quantities of acid are significant (e.g., a reservoir 8000 ft below the surface capable of storing 1.0 BCF of natural gas would require 1.8% of the nations hydrochloric acid production in 2002); therefore, it is very likely that the negotiated price for acid would be 10 to 50% less than the current market price for technical grade hydrochloric acid. Additionally, Figure 8 shows current sales prices for a variety of calcium chloride products. It was assumed for the overall cost estimate that only 75% of the calcium chloride product could be recovered and sold as 80% flake product. The exact purity and form of the calcium chloride product leaving the clarifier could vary with process conditions and with the location of the two wells (i.e., the presence of impurities in the underground limestone could affect the purity of the precipitated $CaCl_2$ product).

Table 7. Estimated fixed capital cost factors for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid.

Operation	**Lang Factors, Solid-Liquid (Peters and Timmerhaus, 1991)**	**Cost ($ US)**
Direct Costs		
Purchased equipment	100	799,640
Installation	39	311,860
Instrumentation	13	103,953
Piping	31	247,888
Electrical	10	79,964
Buildings	29	231,896
Yard Improvements	10	79,964
Service facilities	55	439,802
Land	2	15,993
Indirect Costs		
Engineering & Supervision	32	255,885
Construction expenses	34	271,878
Contractor's fee	18	143,935
Contingency	36	287,871
Total Fixed Capital Investment	**407**	**3,270,529**

Table 8. Estimated delivered equipment costs for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid.

Purchased Equipment	**Cost ($ US)**
Clarifier, (for con. $CaCl_2$ solution)	449,640
Sealless, acid-resistant centrifugal pumps	85,000
Hydrochloric acid storage tanks	265,000
Wetlands treatment area	30,000
Total Equipment Costs (delivered)	**799,640**

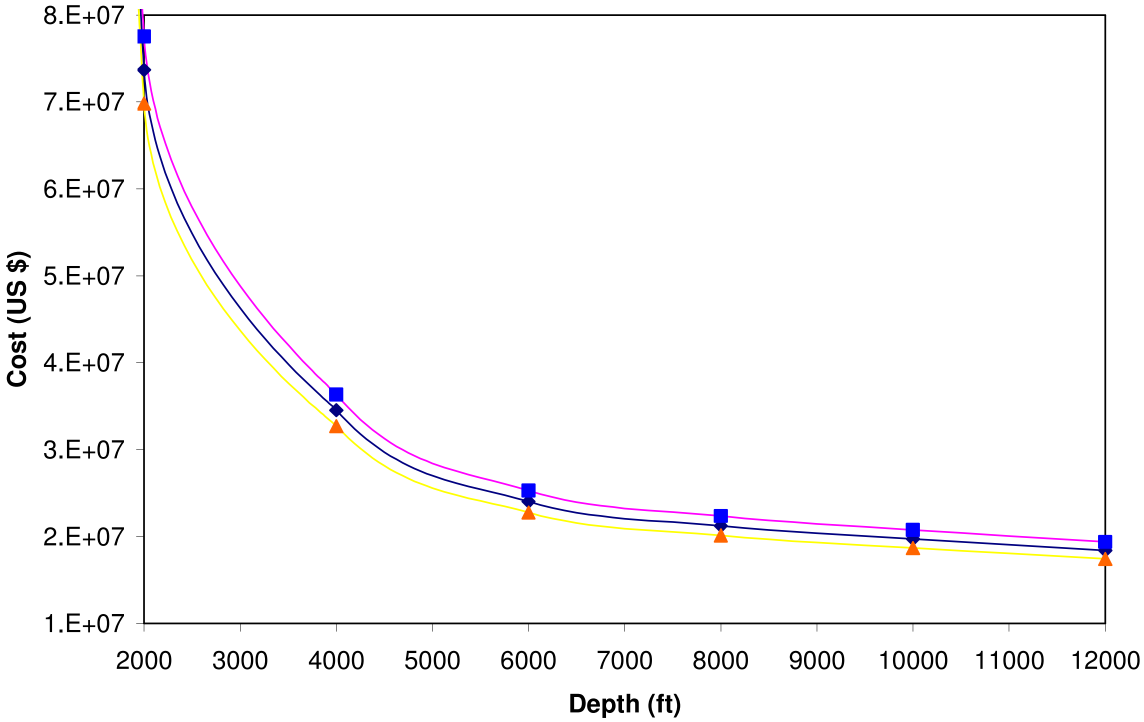


Figure 7. Cost of aqueous HCl (33 wt% solution) needed for a 0.5 BCF natural gas storage facility at varying depths in the northeastern US.

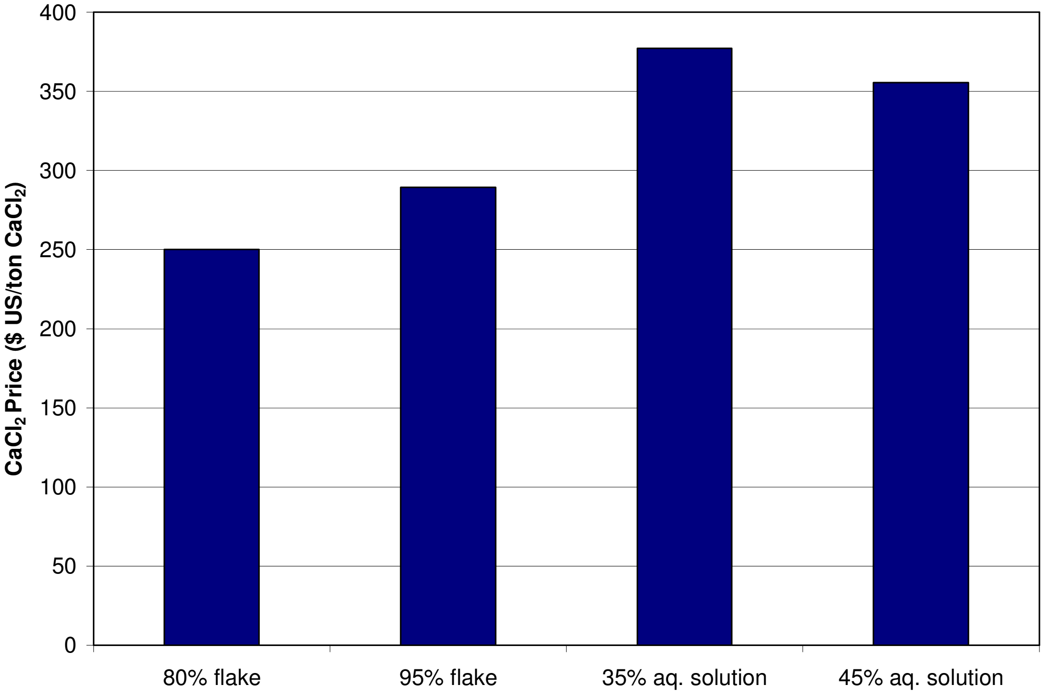


Figure 8. Commercial scale sales price for CaCl2 in various forms and concentrations. (Chemical Market Reporter, Dec. 2003).

Estimation of Total Facility Costs

The total gross-earnings cost for developing an underground gas storage facility via the acid dissolution of limestone equals the difference between total income derived from the sale of calcium chloride salts minus the total development cost. The total development cost for the gas storage facility can be estimated by summing the direct production costs, fixed charges, and facility overhead charges. The factors for these various costs were taken from the text by Peters and Timmerhaus (1991) and are a primarily a function of the hydrochloric acid cost, and the total capital investment cost. These economic factors are reported in Table 9 and the total gross-earnings cost for a 0.25 or 0.5 BCF gas storage facility in limestone is shown in Figure 9 as a function of limestone porosity at depth. Though no data are presented in this report on dolomite dissolution costs (for brevity), these costs were evaluated and found to be approximately 6% more than that for limestone formations. This is primarily due to the higher density of the dolomite rock as compared to limestone.

Table 9. Estimated total production cost factors for a 0.5 to 1 BCF gas storage facility created via acid dissolution of limestone using hydrochloric acid.

Item	% Total Development Cost
Direct Production Costs	
Raw Materials	49
Labor	14
Utilities	8
Maintenance	3
Fixed Charges	
Depreciation - Fixed Capital Cost	9
Taxes	1.5
Insurance	0.5
Plant overhead	8
General Expenses	
Administration Costs	2
Distribution and selling costs	5
Total	100

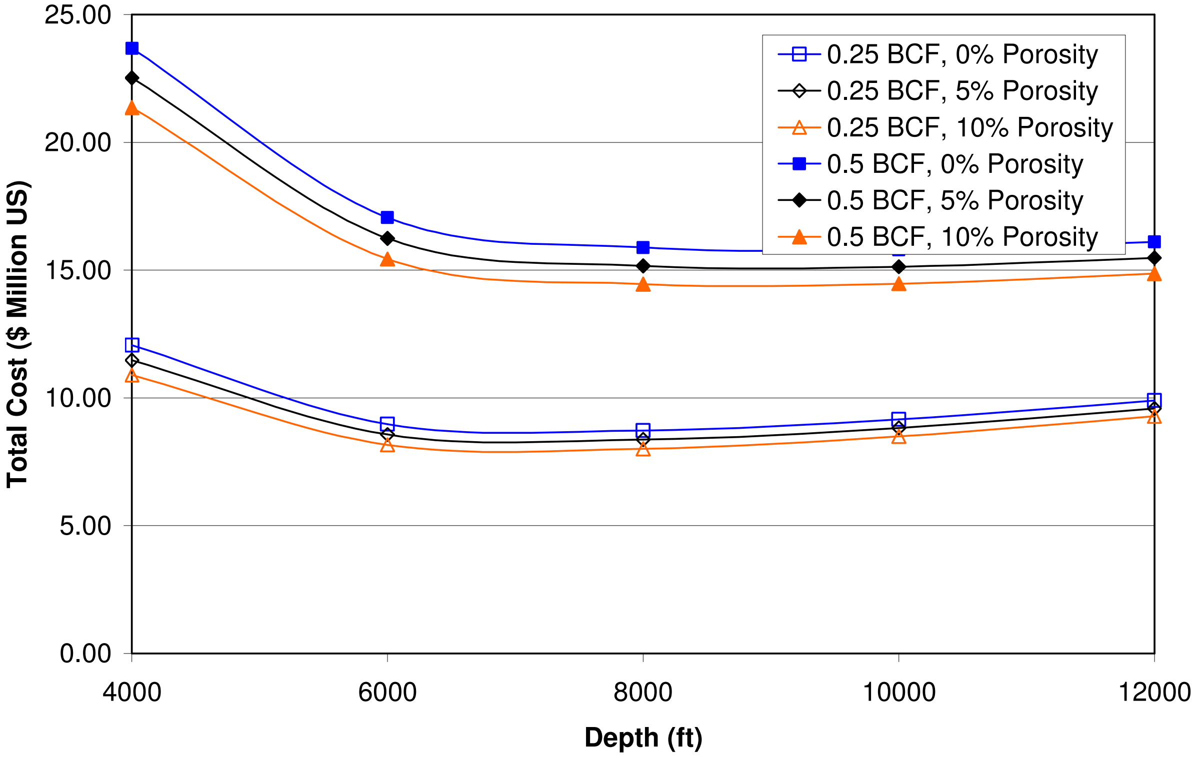


Figure 9. Total cost for a 0.25 and 0.5 BCF natural gas storage facility in limestone of varying porosity at varying depths in the northeastern US.

Comparison of Gas Storage Costs

There exist several possibilities for increasing the availability of natural gas storage near major use markets. Some (but not all) of the possibilities are depicted in Figure 10 and include: 1) construction of new above ground gas storage vessels of varying size, 2) conversion of abandoned mines to underground gas storage facilities, 3) conversion of existing aquifers to gas storage facilities, and 4) the development of new underground gas storage facilities via the dissolution of rock (this proposal) or salt. With each of these methods there are both economic and safety considerations. The construction of large numbers of above ground gas storage vessels introduces considerable risk in the modern era of terrorism. The most feasible way to store gas above ground is to liquefy it, which is expensive, and then store it in insulated tanks as liquefied natural gas (LNG). The conversion of abandoned mines to underground gas storage facilities suffer from the fact that the mines may not be located near existing gas storage pipelines or population centers. Additionally, these mines may not be suitable for storing the natural gas because of the many containment issues of abandoned mines.

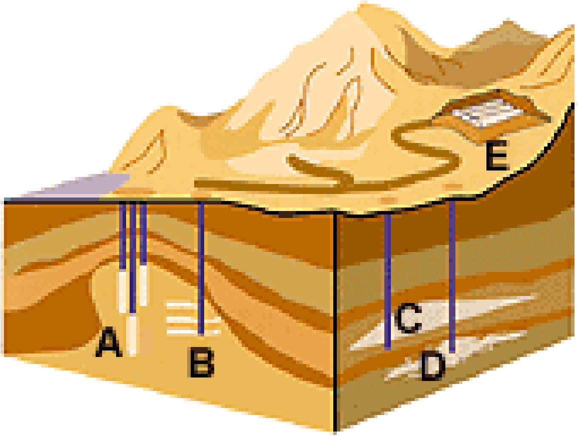
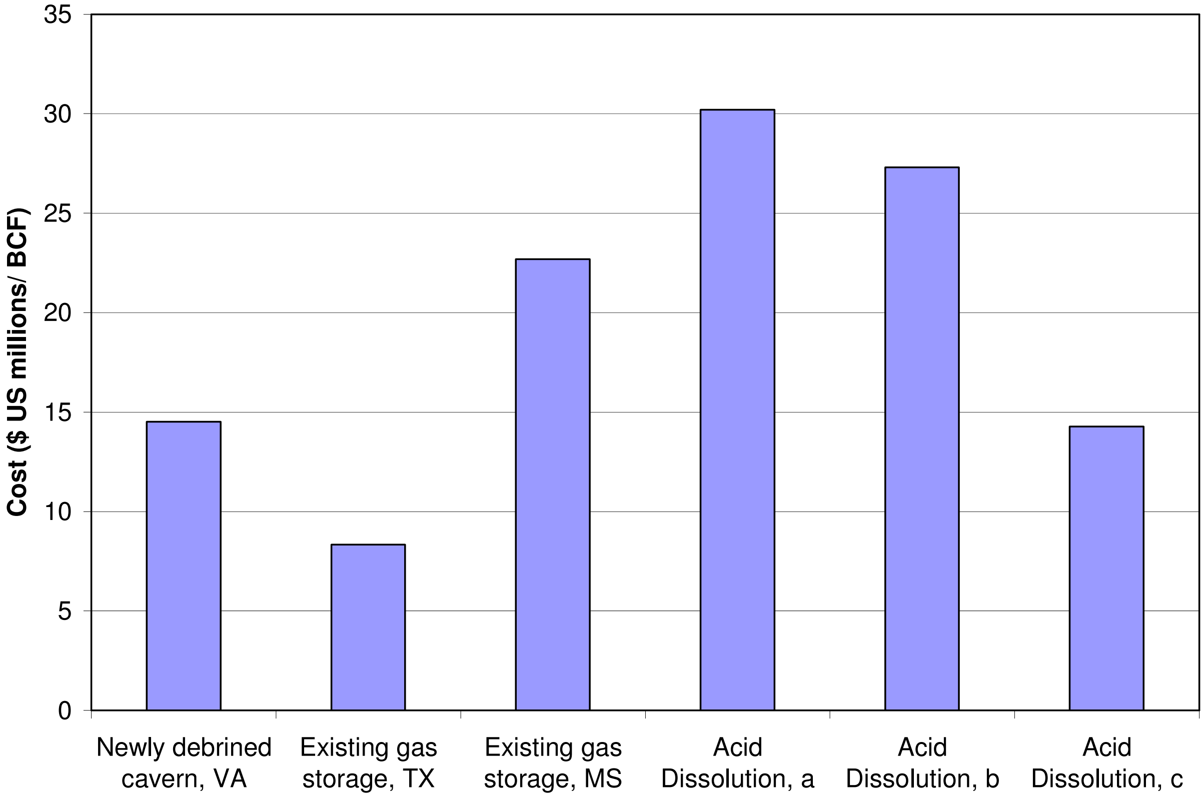


Figure 10. Types of underground natural gas storage: A) salt caverns, B) mines, C) aquifers, D) depleted oil/gas reservoirs, and E) hard rock mines. From www.fe.doe.gov/programs/oilgas/storage.

In order to evaluate the economic feasibility of the limestone dissolution process, cost comparisons were made to existing or newly created underground gas storage facilities and are shown in Figure 11. This figure shows cost for salt storage and storage created using the new fracturing and acid-dissolution process. More detailed cost information is provided in Appendix A. The total gross-earnings cost analysis shows that reductions in cost are achieved with increases in rock porosity and are significantly influenced by the sales price of hydrochloric acid and calcium chloride. If hydrochloric acids costs can be negotiated to a value lower than the average list sales price, then the new process is even more competitive with other means for creating underground gas storage. Such reductions in acid cost are very likely given the quantity of acid to be purchased and the ability to use low purity hydrochloric acid. For example, Reed Business Information's Online Purchasing Magazine lists hydrochloric acid sales prices as low as $58 per metric ton for technical grade acid – a 23% reduction in acid cost over that used for the primary cost estimates in this report.

Optimum Rock Formations

The gross earnings costs clearly indicate the advantages of developing limestone storage caverns at depths greater than 4000 ft, where natural gas densities are near their maximum. Additionally, the increased density of dolomite deposits requires that more acid be use to develop storage in these rock formations. Thus, the preferred rock formation is one made of limestone at depths between 6000 and 9000 ft. Further cost savings (up to 9%) can be achieved by developing gas storage in limestone with increased porosity (up to 15%). Such limestone deposits exist in several regions of the US (discussed later) and similar gas storage fields have been developed within this depth range (American Gas Association, 2002).



a 1 BCF, 0% Porosity, Listed Acid Cost, 75% CaCl2 sold, 8000 ft.
b 1 BCF, 10% Porosity, Listed Acid Cost, 75% CaCl2 sold, 8000 ft.
c 1 BCF, 5% Porosity, 65% of Listed Acid Cost, 75% CaCl2 sold, 8000 ft.

Figure 11. Cost comparison between various underground gas storage methods.

Regional Survey of Carbonate Formations (Task 4)

Identification of Carbonate Units and Regional Stratigraphic Analysis

A regional survey was conducted to identify carbonate formations that are likely candidates for developing gas storage using the fracturing and acid-dissolution method. In consultation with DOE, the following states were selected for the regional survey: Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York. Thick, laterally continuous carbonate sequences underlie major portions of these states. To identify the regional extent of each of these units, a series of maps was produced. Existing data were used primarily for this task.

Using the COSUNA charts for the northern and southern Appalachian Basins (Patchen et al., 1984a, 1984b) and Rupp (1991) for Indiana, seven major carbonate units were identified for mapping in each of the selected states (Table 10). These carbonate units are generally separated by non-carbonate (siliciclastic or evaporate) formations, which may help provide an overlying seal for the fracturing and acid-dissolution process. The only common exception to the presence of non-carbonate directly overlying the carbonate unit is the contact between Units 5 and 6. In a few areas, Unit 6 directly overlies Unit 7.

The approximate values for ranges of porosity and permeability are listed in Table 11 for the carbonate units mapped. Although published values of porosity and permeability were found to be very sparse, depth and thickness values were available from the state geological surveys for most areas and were used for mapping. The porosity ranges in Table 11 include values that are equivalent to optimum values for generating storage capacity using the fracture-acid dissolution method (see the section on "Process Design and Economics" in this report).

Table 10. Regionally correlative and mappable carbonate units in the project area and their geologic age. In Indiana, Unit 4 includes the entire Silurian section because of the extensive deposition of carbonate sediment during that time.

Carbonate Unit	Age
1	Early Mississippian
2	Middle Devonian
3	Late Silurian – Early Devonian
4	Late Silurian (Silurian in Indiana)
5	Late Ordovician
6	Late Ordovician
7	Late Cambrian – Early Ordovician

Table 11. Approximate values for ranges of porosity and permeability of the carbonate units mapped. Data from Wickstrom at al. (1992); Riley et al. (1993); Roen and Walker (1996).

Carbonate Unit	Porosity Range (%)	Permeability Range (md)
1	0 - 27	0 - 1
2	2 - 10	0 - 600
3	2 - 10	not found
4	2 - 20	0 - 54
5	1 - 20	0.3 - 9000
6	1 - 14	0.3 - 9000
7	0 - 22	0 - 56

The carbonate formations included in each of the mapping units and the non-carbonate formations separating the mapping units are listed in Tables 12-17. The formations are listed in the correct stratigraphic position. In addition, the predominant lithology in each carbonate unit is listed. Not all of the carbonate units are present in all six states because of regional variations in deposition and erosion. Some comments regarding the stratigraphy in each state follow.

Indiana

The Salem Limestone of Indiana is stratigraphically equivalent to the Greenbrier Group and Newman Limestone of the other states (John Rupp, Indiana Geological Survey, personal communication). In Indiana there is no specific, equivalent formation to the Silurian-Devonian carbonates (i.e., the Helderberg Group). The Lower Devonian New Harmony Group is mainly chert, and the Silurian section is almost entirely carbonate. For this reason, Unit 3 in Indiana is not mapped and the entire Silurian section is assigned to Unit 4.

Kentucky

Because the Kentucky Geological Survey groups the Onondaga Limestone and Helderberg Limestone together in their database, Units 2 and Unit 3 are combined in Table 13. These formations in Kentucky are commonly difficult to differentiate using cores or logs.

New York

In general, the sedimentary units in New York are at their deepest along the southern border of the state and dip upwards toward the surface in north central New York. In New York, Unit 1 is not present and thus was not mapped.

Ohio

Data for Ohio were obtained through the Ohio Geological Survey in the form of digital data files (DDFs) that can downloaded from their website. DDF 1 contains data for northwestern Ohio and DDF 2 contains data from the eastern half of Ohio. These files were merged to produce a composite map for the state. While these digital files contain many wells, the formation top data are limited. In particular, the data for formations above the Ordovician are sparse. Apparently, based on enquiries to personnel at the Ohio Survey, more data will become available to the public after their work in progress has been completed. As a result, the only formation above the Trenton that could be mapped was the Onondaga (Unit 2), and only a top for that formation could be obtained. Thus Units 3 and 4 could not be mapped. Unit 1 is generally not present in Ohio.

The stratigraphy of Ohio is complicated by the presence of the Findlay Arch, which cuts approximately across the middle of the state and then merges with the Cincinnati Arch in the southwestern part of the state.

Pennsylvania

Most units are at their shallowest depth in the northwest corner of the state and become progressively deeper eastward into the Appalachian basin. The carbonate units become difficult to map near the structural front because of complexities such as thrust faults. For a few wells near the structural front, some formations are listed in the data base as many as four times due to thrust stacking. In these cases, depth of the deepest occurrence was mapped. Thickness of repeated section due to thrusting was used for mapping thickness only if there were no intervening non-carbonate layers. Unit 1 is not present in Pennsylvania and thus was not mapped.

Because a siliciclastic unit (Upper Sandy Member) is present consistently within Unit 7 in Pennsylvania, this unit is divided into Subunits 7a and 7b for mapping purposes.

West Virginia

In West Virginia, Unit 3 was divided into Subunits 3a and 3b because of the intervening Big Mountain Shale. Subunit 3a corresponds to the Helderburg Group and Subunit 3b to the Tonolaway Limestone.

Table 12. Geologic formations and predominant lithology of carbonate units in Indiana.

Unit	Formation(s)	Lithology of Carbonate Units
1	Salem Limestone	Limestone
	Borden Group New Albany Shale	-
2	Muscatatuck Group	Limestone, grades to dolomite in northeast
3	not present	-
4	Bainbridge Group Sexton Creek Limestone	Limestone
	Maquoketa Group	-
5	Trenton Limestone	Limestone, grades to dolomite in north
6	Black River Group	Limestone, grades to dolomite in northwest
	Ancell Group	-
7	Knox Group	Dolomite

Table 13. Geologic formations and predominant lithology of carbonate units in Kentucky.

Unit	Formation(s)	Lithology of Carbonate Units
1	Newman Limestone	Limestone
	Upper Devonian Shales	-
2/3	Onondaga Limestone Helderberg Limestone	Limestone
4	Salina Formation Lockport Dolomite	Dolomite
	Keefer Sandstone Rose Hill Formation Juniata Fm./Drakes Fm.	-
5	Lexington Ls. (Trenton Ls.)	Limestone
6	High Bridge Gp. (Black River Gp.)	Limestone
	St. Peter Sandstone	-
7	Knox Group	Dolomite

Table 14. Geologic formations and predominant lithology of carbonate units in New York.

Carbonate Unit	Formation(s)	Lithology of Carbonate Units
1	not present	-
2	Onondaga Limestone Bois Blanc Limestone	Limestone
	Oriskany Sandstone	-
3	Helderberg Group Roundout Formation Bertie Formation Cobleskill Limestone Bass Islands Group	Predominantly Limestone, Minor Dolomite
	Salina Group	-
4	Lockport Group	Dolomite/Limestone
	Clinton Group Medina Group Queenston Formation	-
5	Trenton Group	Limestone
6	Black River Chazy Fm./Wells Creek Fm.	Limestone
	Glenwood Shale	-
7	Beekmantown Group Tribes Hill Formation Little Falls Formation Theresa Formation Copper Ridge Formation	Dolomite/Limestone

Table 15. Geologic formations and predominant lithology of carbonate units in Ohio.

Unit	Formation(s)	Lithology of Carbonate Units
1	not present	-
	Upper Devonian Shales	-
2	Onondaga Limestone	Limestone
	Oriskany Sandstone	-
3	Helderberg Limestone Keyser Limestone Bass Islands Group	Limestone
	Salina Group	-
4	Lockport Dolomite	Dolomite
	Clinton Group Albion Group Undifferentiated shales	-
5	Trenton Limestone	Limestone
6	Black River Group Gull River Fm. Wells Creek Fm.	Limestone
7	Knox Group	Dolomite

Table 16. Geologic formations and predominant lithology of carbonate units in Pennsylvania.

Carbonate Unit	Formation(s)	Lithology of Carbonate Units
1	not present	-
2	Onondaga Limestone Bois Blanc Formation Buttermilk Limestone	Limestone
	Huntersville Chert Oriskany Sandstone	-
3	Helderberg Limestone Keyser Formation Bertie Dolomite Tonolaway Limestone Bass Islands Dolomite	Predominantly Limestone, Minor Dolomite
	Salina Group	-
4	Lockport Dolomite McKenzie Member	Dolomite/Limestone
	Clinton Group Tuscarora Sandstone Reedsville Shale	-
5	Trenton Limestone	Limestone
6	Black River Group Loysburg Formation Shadow Lake Formation	Limestone
7a	Knox Group Upper Gatesburg Formation	Dolomite/Limestone
	Upper Sandy Member	-
7b	Lower Gatesburg Formation Warrior Formation Pleasant Hill Formation	Dolomite/Limestone

Table 17. Geologic formations and predominant lithology of carbonate units in West Virginia.

Unit	Formation(s)	Lithology of Carbonate Units
1	Greenbrier Limestone (Big Lime)	Limestone
	Upper Devonian Shales	-
2	not present	-
	Oriskany Sandstone	-
3a	Helderberg Group	Limestone
	Big Mountain Shale	-
3b	Tonolaway Limestone	Limestone
	Salina Formation	-
4	Lockport Dolomite	Dolomite
	Keefer Sandstone Rose Hill Formation Tuscarora Sandstone Juniata Fm. Martinsburg Fm.	-
5	Trenton Limestone	Limestone
6	Black River Group Wells Creek Formation/ St. Paul Gp./Chazy Fm.	Limestone
	St. Peter Sandstone	
7	Knox Group	Dolomite

Data Management: Selection, Filtering, and Quality Assurance

Well data, including formation tops, were obtained from the state geological surveys. The goal of the data selection process was to obtain an even distribution of wells throughout each state. Typically, a spreadsheet or shapefile of deep oil and/or gas wells was obtained and displayed in a GIS program (ArcView). The wells were sorted by depth, and then a manageable number of wells (typically 200 – 300) were selected manually and using spatial analysis techniques. This list of wells was then submitted to the appropriate state survey representative, who would return a list of formation tops for each well. In most cases, not all of the wells submitted would have formation tops, as some of the older wells were drilled before well logging and required reporting. A second method of obtaining data was to submit a list of the carbonate formations to the state survey representative, who would then provide all the wells with those formations.

The formation data were imported into an Excel spreadsheet and processed using a variety of techniques. The data came in a multitude of formats, as each state has its own unique database and way of storing and presenting the data. The task of separating the data into a consistent format for incorporation into a GIS database was done manually. During this process, obvious errors were deleted. Once the data were converted into a GIS database and displayed, spurious data were eliminated using spatial analysis and manual methods. For example, when spatial interpolation was used to create surfaces of the formation tops and thicknesses, the anomalous points could be visually identified and examined for possible removal from the mapping database.

The following is a summary of the steps followed in the preparation and analysis of the geologic data:

1) Obtained geologic data (i.e., formation tops) from state geological surveys;
2) Put all data into a consistent format;
3) Loaded data into GIS;
4) Constructed DEMs (digital elevation models) for each state;
5) Created surface on each formation top (point data were converted to a grid surface);
6) Created depth surfaces from ground surfaces and formation top surfaces;
7) Converted depth surfaces to contours;
8) Created and contoured formation thickness maps;
9) Generated maps showing occurrence of carbonate units and limestones for specific depth intervals.

Mapping and Analysis of Depth and Thickness Data

Once data selection and quality control were completed, the formations were ready for mapping. A digital elevation model (DEM), which is essentially a topographic map of the ground surface, was constructed for each state. Each statewide DEM has a 90-meter resolution and was created by combining smaller 1-degree DEMs obtained from the USGS. The DEMs were originally in geographic coordinates (latitude-longitude), which creates slightly distorted grid cells. The grid distortion problem was solved by converting the grids to the Lambert Conformal coordinate system.

Maps showing the depth from the ground surface to the top of each carbonate unit were constructed within a GIS framework using map algebra techniques. Carbonate unit elevation (structural) tops were interpolated into surfaces, and the resulting surfaces were subtracted from the state DEMs to produce maps showing the depth to the top of each carbonate unit. The thickness of each unit was then interpolated. The depth surfaces and thickness values were contoured. The depth maps are shown in Figures M1- M35 ; the thickness maps are shown in Figures M36 - M69.

The depth ranges and thicknesses of the carbonate units in each state are listed in Tables 18 and 19, respectively.

Table 18. Depth range to the top of mapped carbonate units for each state. Depths are in feet.

Unit	Indiana	Kentucky	New York	Ohio	Penn.	W. Virginia
1	1000-3500	500-4000	Not Present	Not Present	Not Present	500-3000
2	500-4500	2000-4500	1000-4000	500-4500	2000-9000	Not Present
3	Not Present	2000-4500	1000-5000	No Data	2000-9000	2000-7000
4	500-5000	500-5000	1000-6000	No Data	3000-9000	4000-10000
5	1000-6000	1000-7000	1000-9000	2000-8000	4000-15000	6000-13000
6	1000-6000	1000-6000	1000-10000	2000-9000	5000-16000	6000-14000
7	1000-7000	1000-8000	1000-10000	2000-10000	6000-16500	4000-14000

Table 19. Thickness range of mapped carbonate units for each state. Thicknesses are in feet.

Unit	Indiana	Kentucky	New York	Ohio	Penn.	W. Virginia
1	200-700	100-400	Not Present	Not Present	Not Present	100-900
2	200-1400	100-170	50-800	No Data	50-250	Not Present
3	Not Present	100-170	100-900	No Data	200-1200	100-1000
4	300-800	50-300	100-500	No Data	500-3500	100-500
5	50-300	200-800	100-1100	40-280	200-900	200-1100
6	200-800	500-1200	100-700	350-800	400-2200	800-1800
7	500-3500	1500-4500	200-1600	200-1000	500-5000	1300-2900

Identification of Geologically Suitable Areas for Applying the Technology

As discussed in a previous section of the report (see the section on “Optimum Rock Formations”), design considerations and economic calculations indicate that the fracturing and acid-dissolution method will be applied most advantageously to carbonate formations deeper than 4000 feet, with limestone at depths between 6000 and 9000 feet preferred. In order to identify areas that are potentially suitable for applying the fracture-acid dissolution technology to creating storage volume, a series of maps was produced using carbonate depth and thickness criteria. Figures M70-M93 show the areas in which carbonate units occur that have a minimum thickness of 300 feet. To further refine the areas identified as being potentially suitable for using the fracture acid-dissolution method, maps were generated to identify areas of limestone having a minimum thickness of 300 feet (Figures M94-M111). Four depth ranges were selected for producing each series of maps, which are called “suitability maps”:

1) 4000 to 6000 feet;
2) 6000 to 8000 feet;
3) 8000 to 10,000 feet; and
4) 10,000 to 12,000 feet.

The suitability maps show that there are carbonate units at a suitable depth present in specific areas of all six states of the project area. Large areas of Pennsylvania, West Virginia, and New York are potentially suitable geologically for developing gas storage using the fracturing and acid-dissolution method. Smaller areas with the optimum thickness and depth of carbonate rocks for using the technology are present in the other states. These maps depict the best areas for using the fracture-acid-dissolution method based on unit thickness and depth; carbonate units at other depths are present in all 6 states, which open up additional areas for using the technology under with sufficient demand for storage. It’s likely that potential areas for development of the new technology are present in additional areas of some of the states because not all areas could be mapped due to lack of well control (e.g., Units 6 and 7 in West Virginia; Figures M68 and M69). Of course, specific geologic properties should be examined in greater detail than was done in this regional analysis before applying the technology in any of the areas mapped.

Current Modeling Technology (Task 5)

A detailed report on current modeling technology, which is being transmitted separately, summarizes the extent of information available on existing technology that is relevant to the fracturing and acid dissolution modeling that will be done in the next phase of the project.

The main programs that we plan to use for the fracture modeling are FRANC2D and HFRANC2D (Tan et al., 2003). HFRANC2D is a flexible, fracture modeling code that has been adapted to account for internal fluid flow during hydraulic fracturing. The dissolution approach involving circulation between two wells will be enabled by linking hydraulic fractures created from the wells. Simulating the linking of two hydraulic fractures requires a code that can predict curved propagation paths, which can be done by HFRANC2D. FRANC2D, which is used to calculate stresses and displacements by HFRANC2D, has recently been used to study the interaction of neighboring cracks by Sim et al. (2003).

We plan to use specialized versions of the Lawrence Berkeley National Laboratory (LBNL) TOUGH codes to perform numerical simulation of the limestone dissolution process. Detailed simulation of the limestone dissolution geochemistry and resulting fluid phase behavior will be performed using the TOUGHREACT/ECO2 code. TOUGHREACT/ECO2 in an internal LBNL simulator developed by Xu et al. (2003) and Xu and Pruess (1998). This code is based on the TOUGHREACT module for TOUGH (Xu and Pruess, 1998) that couples complex equilibrium and kinetic geochemistry (including kinetic mineral dissolution and precipitation with permeability changes) with three-dimensional, two-phase, non-isothermal flow. This code, like all of the TOUGH codes, is applicable to complex fractured and heterogeneous porous media. TOUGHREACT is currently being applied to a variety of difficult geochemistry/multiphase flow problems ranging from CO_2 sequestration to ore body genesis, to high-level radioactive waste isolation. Of particular interest here is the recent coupling of the ECO2 module (Pruess and Garcia, 2002) with TOUGHREACT. The ECO2 module for TOUGH provides a comprehensive thermodynamic treatment of the phase behavior of supercritical CO_2. This is significant in the current work because the dissolution process will take place at depths of at least 1000 m, where the pressure and temperature will both be well above the critical point for CO_2 (T_{crit}=31.04 ^oC; P_{crit}=73.82 bar). As each kg of limestone is dissolved by the acid, approximately 0.44 kg of CO_2 will be produced. Depending on the rate of rock dissolution, CO_2 is likely to evolve as a separate supercritical phase in the subsurface. TOUGHREACT/ECO2 is the only code capable of considering this complex interplay between multiphase flow, geochemistry, and supercritical CO_2 phase behavior.

One area that will need to be addressed in the upcoming year will be the numerical treatment of fluid flow in the open cavern or fissures, as well as the associated mass transfer of acid and dissolved rock products to and from the rock face. TOUGHREACT/ECO2 and the other TOUGH codes use Darcys law to describe the multiphase flow. As a first approximation, we will assign very high intrinsic permeability to zones where the rock has completely dissolved away. The mass transfer will be initially simulated with local equilibrium in each gridblock, with mass transfer at larger scales occurring by inter gridblock flow and transport. We plan to use a somewhat simplified 3-D numerical model of the limestone dissolution process (a slightly modified version of T2VOC (Falta et al., 1995) to explore different options for modeling the flow and mass transfer processes in open caverns and fissures.

CONCLUSIONS

Results from the first phase of the project indicate that the new method of fracturing and acid dissolution of carbonate rock is a viable process for creating gas storage capacity. The preliminary geologic and economic analysis suggests that the process is competitive when compared with other means of creating underground gas storage. The fracturing and acid-dissolution process has the advantage of being applicable to many different locations, offers high deliverability because of cavernous geometry, and will require a low volume of cushion gas. The method has the potential for leading to commercialization of new gas-storage capacity near major markets. Since depleted gas reservoirs and salt formations are nearly non-existent in many areas, the fracture-acid dissolution process offers an attractive alternative to conventional methods of gas storage.

The following aspects of the fracturing and acid-dissolution process were examined for identifying the requirements for creating storage volume using this process: weight and volume of rock to be dissolved; gas storage pressure, temperature, and volume at depth; rock solubility; and acid costs. Hydrochloric acid was determined to be the best acid to use because of low cost, high acid solubility, fast reaction rates with carbonate rock, and highly soluble products (calcium chloride) that allow for the easy removal of calcium waste from the well. Despite the organic acids offering certain advantages over the inorganic acids, the cost of using any of the organic acids is prohibitive.

The process design and preliminary economics were analyzed by considering capital costs, well-design options and costs, waste treatment options, and comparison with other gas storage costs. The optimum rock type and properties were identified from this preliminary analysis. Results from this phase of the project show that the fracturing and acid-dissolution method is a viable process for creating gas storage. Design considerations and economic calculations indicate that the new method will be applied most advantageously to carbonate formations deeper than 4000 feet, with limestone at depths between 6000 and 9000 feet preferred.

A large amount of data from the carbonate formations in the six-state study area (Indiana, Ohio, Kentucky, West Virginia, Pennsylvania, and New York) were compiled to assess the regional suitability of geological conditions for using the fracture-acid dissolution process. From producing a series of maps using carbonate depth and thickness criteria, large areas of West Virginia, Pennsylvania, and New York are identified as potentially suitable for developing gas storage by using the new technology. Smaller areas are identified in Indiana, Ohio, and Kentucky. Before applying the technology in any of these areas, specific geologic properties should be examined in greater detail than was done in the regional analysis.

The next phase of the investigation will include detailed analysis and modeling of the processes involved in creating storage capacity, including induced fracturing and acid dissolution of the rock. Specific areas, based on the regional analysis completed, will be selected for more detailed geologic characterization of the properties relevant to applying the new technology. The third and final phase of the investigation will include modeling field performance, preparing a final design, and performing an economic analysis. The purpose of the final design is to facilitate full-scale deployment of the new technology. Demonstration of the commercialization potential of gas storage in carbonate rocks will open up new geographic areas for developing storage capacity. The technology is expected to have general application to many geographic areas because of the widespread occurrence of carbonate formations.

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We also thank the personnel of the state geological surveys (Indiana, Kentucky, Ohio, Pennsylvania, New York, and West Virginia) from which data were obtained. In particular, we especially appreciate the time and assistance of the following individuals: Lee Avary (West Virginia Geological Survey), Justin Deming (New York State Museum), John Harper and Cheryl Cozart (Pennsylvania Geological Survey), Dave Harris (Kentucky Geological Survey), and John Rupp (Indiana Geological Survey).

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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

Units of Measure

°Be = Baume
BCF = billion cubic feet
°C = degrees Celcius
°F = degrees Fahrenheit
ft = feet
g = gram
kg = kilogram
km = kilometers
L = liter
lb = pounds mass
m = meters
md = millidarcies
psi = pounds per square inch

Geologic Terms

DEM = digital elevation model
DDF = digital data file
Ls. = Limestone
Fm. = Formation
Gp. = Group
ave = average
perm = permeability
% = percent
K = thousand
#obs = number of observations

Chemical Equations

aq = aqueous solution
C_i = concentration of species *I*
g = gas
ΔG°_{rxn} = Gibbs free energy of reaction
$G^\circ_{f,i}$ = Gibbs free energy of formation
K_{eq} = reaction equilibrium constant
P = pressure
P_{cri} = critical pressure
R = ideal gas constant
s = solid
STP = *standard temperature and pressure*
T = temperature
T_{crit} = critical temperature
V = volume
wt = weight
X = anion
ρ = density

Other

COSUNA = Correlation of Stratigraphic Units in North America
LBNL = Lawrence Berkeley National Laboratory
USGS = United States Geological Survey

Depth to Top of Unit Maps

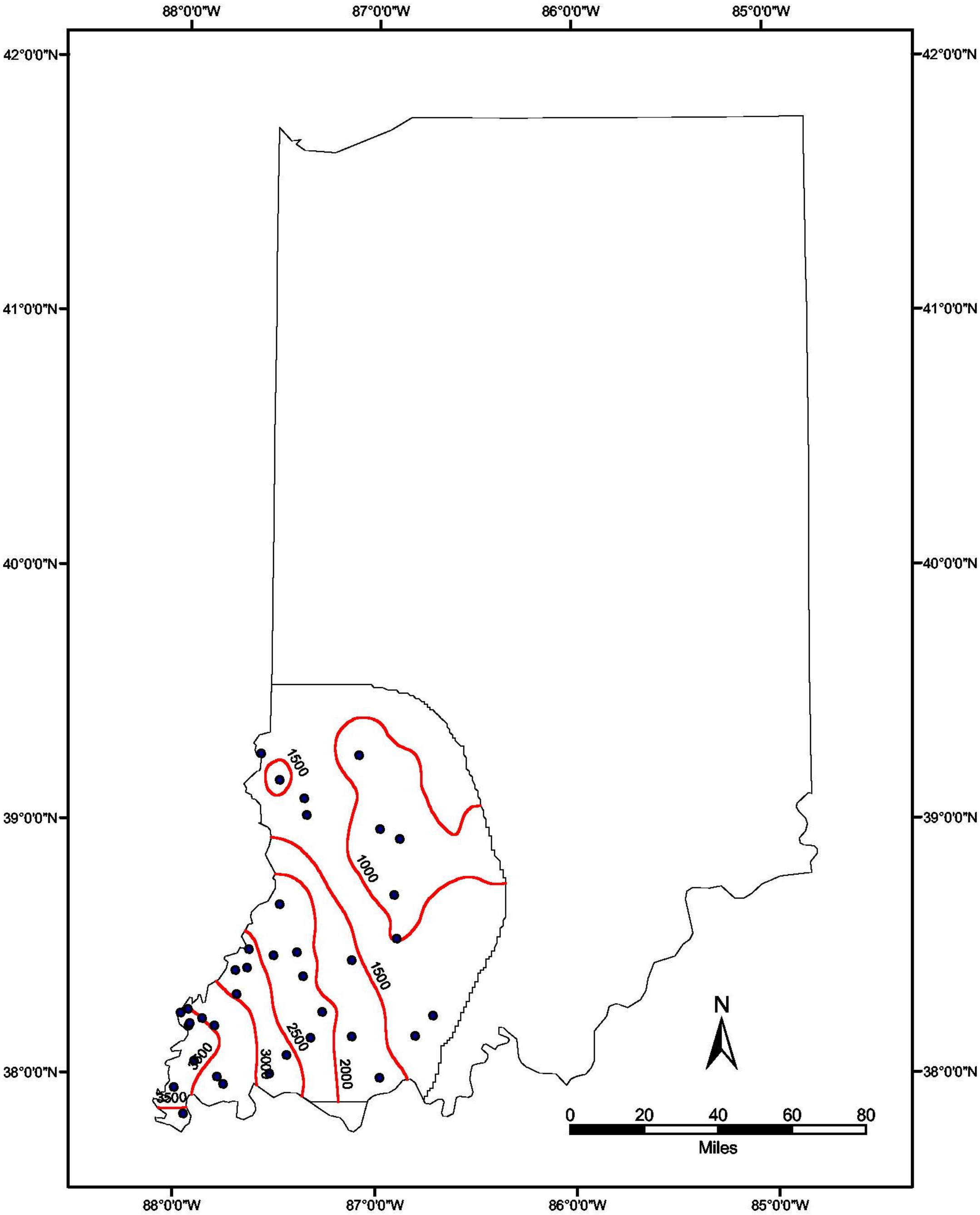


Figure M1. Contour map of depth to top of Unit 1 in Indiana.

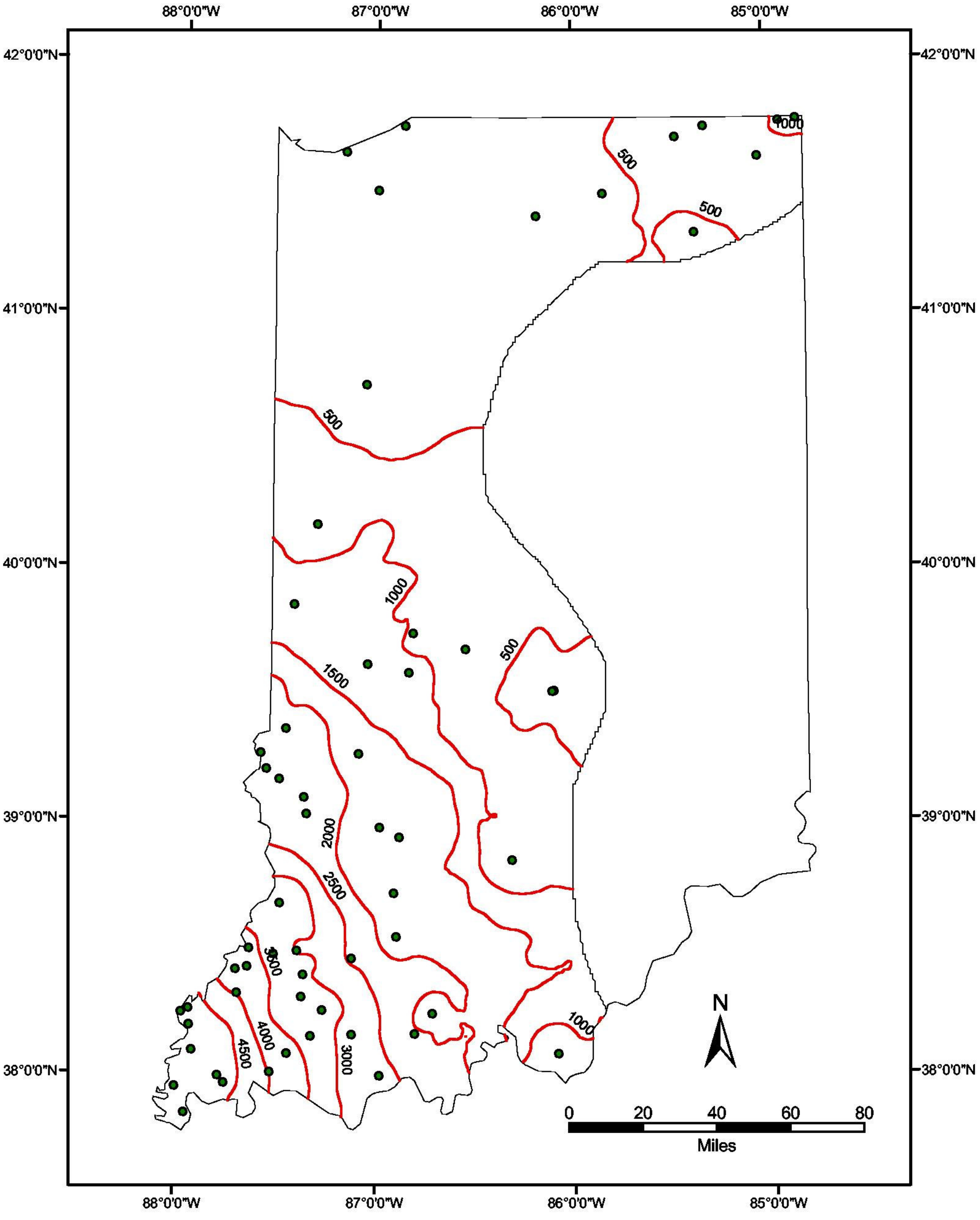


Figure M2. Contour map of depth to top of Unit 2 in Indiana.

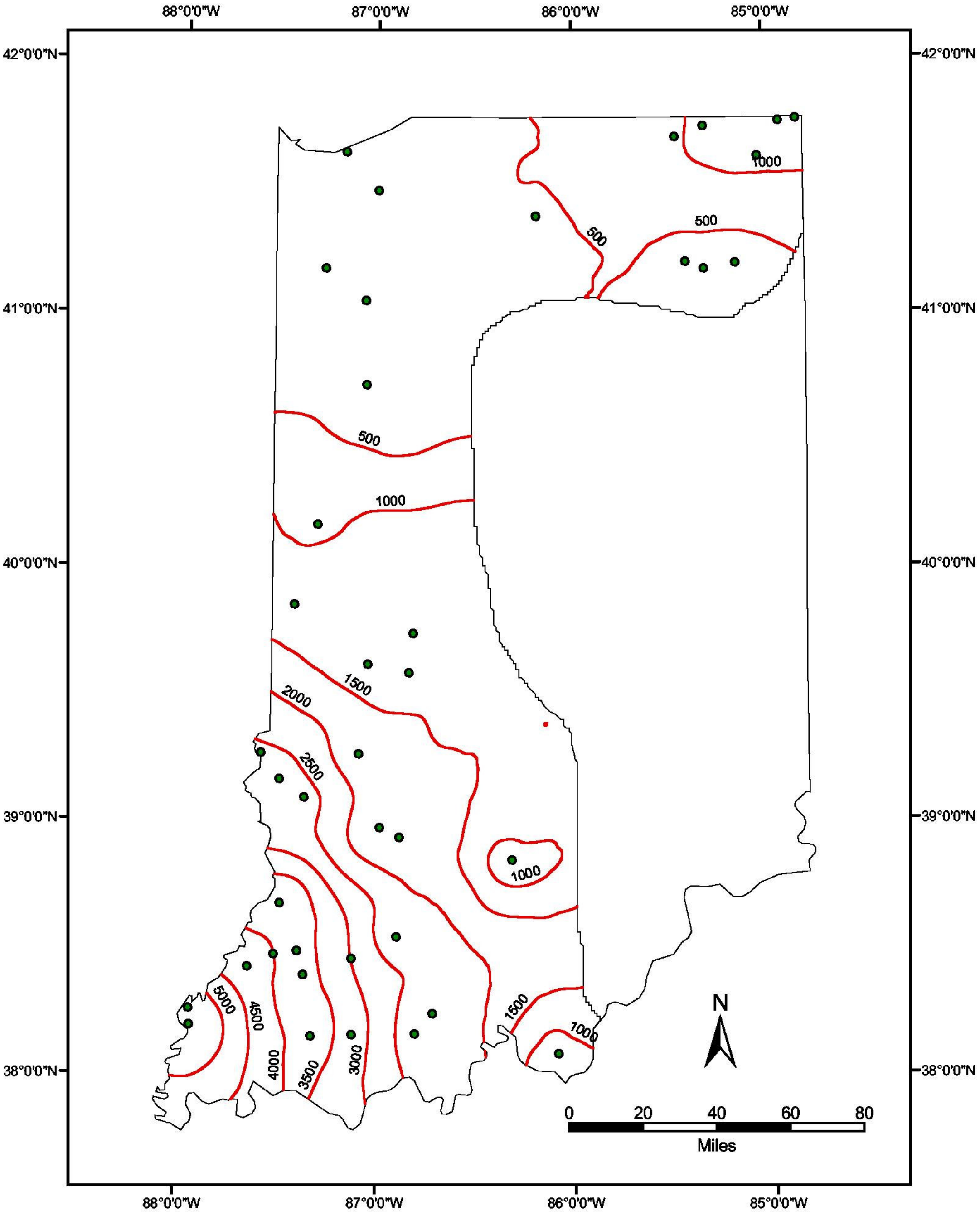


Figure M3. Contour map of depth to top of Unit 4 in Indiana.

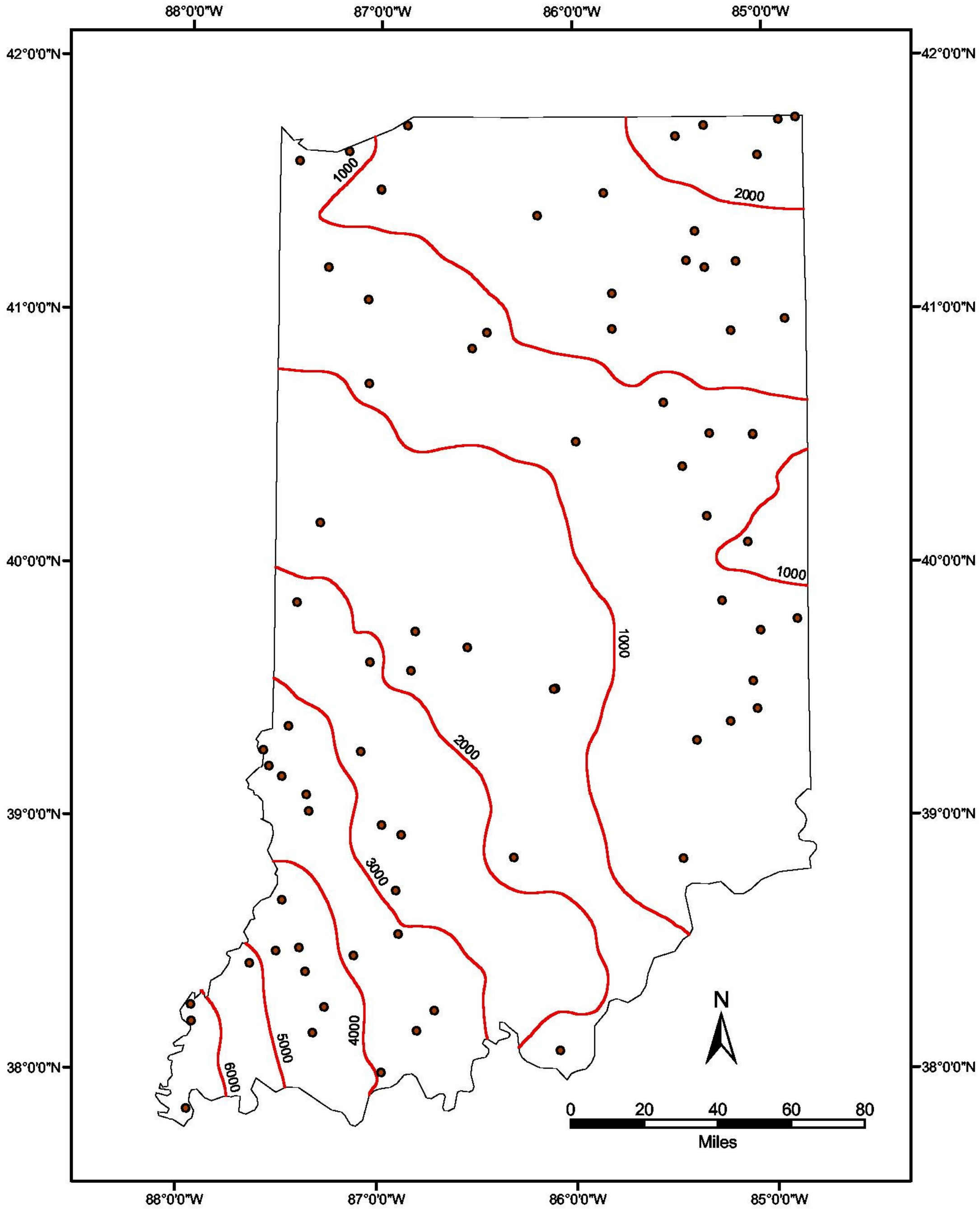


Figure M4. Contour map of depth to top of Unit 5 in Indiana.

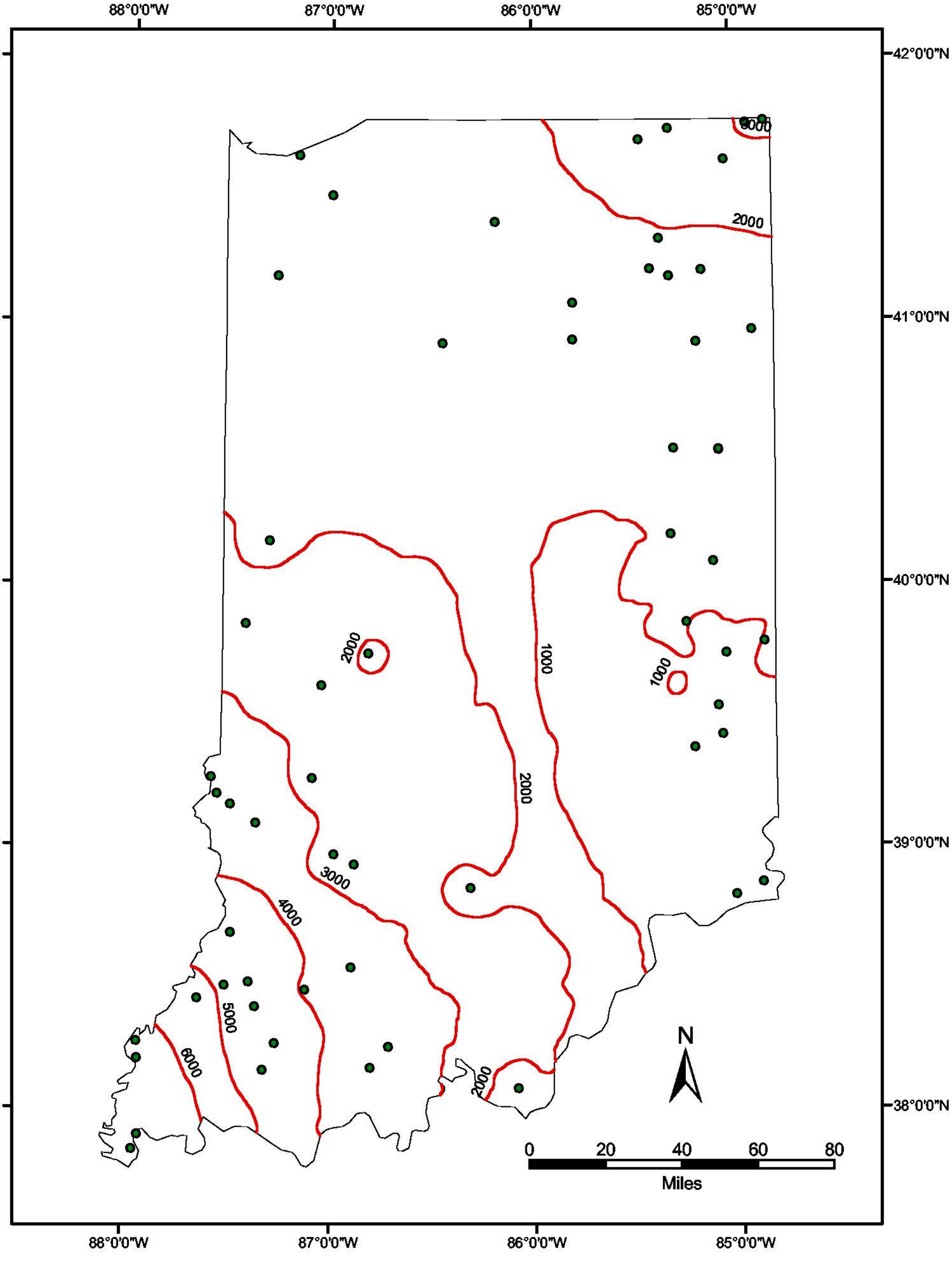


Figure M5. Contour map of depth to top of Unit 6 in Indiana.

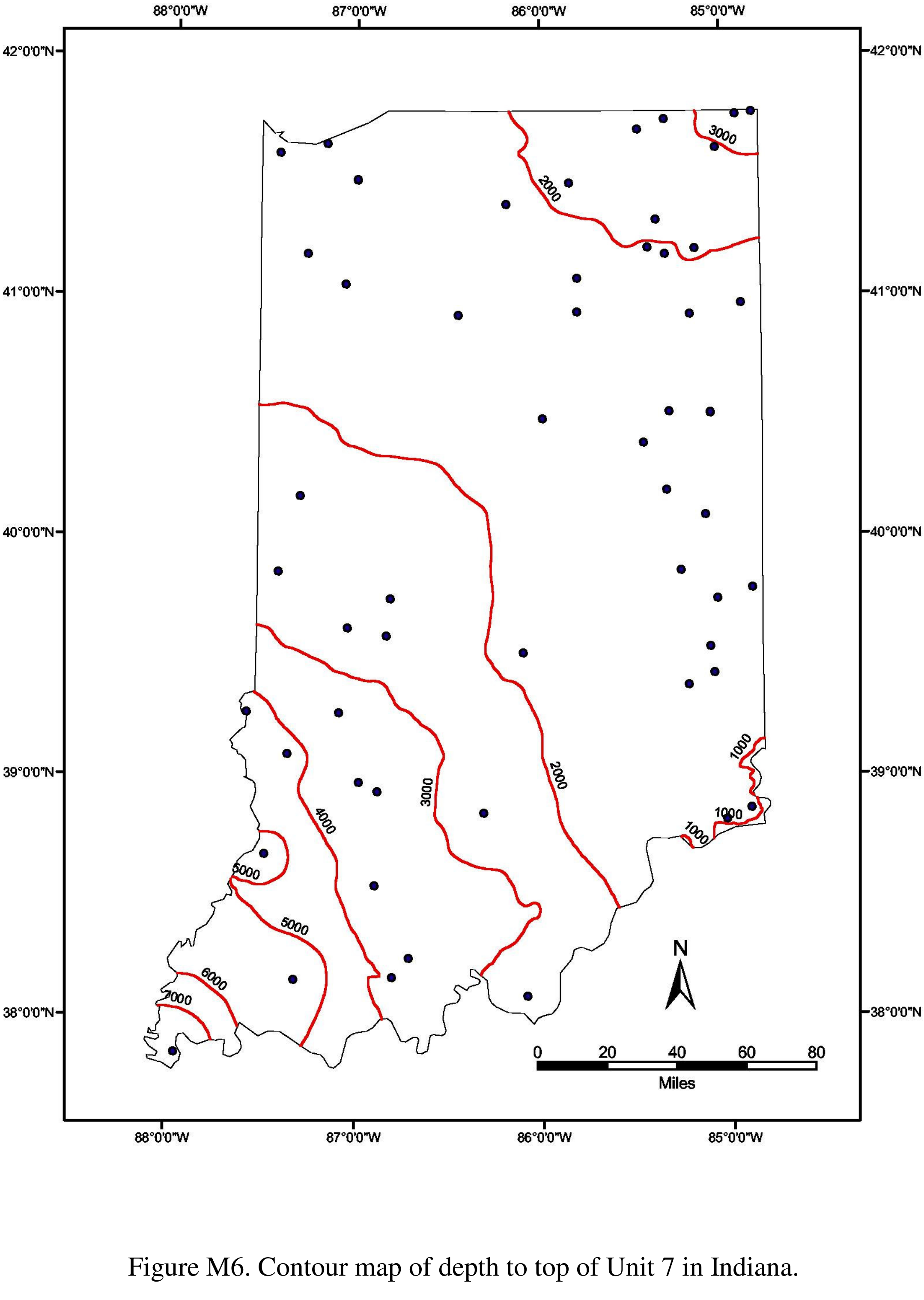


Figure M6. Contour map of depth to top of Unit 7 in Indiana.

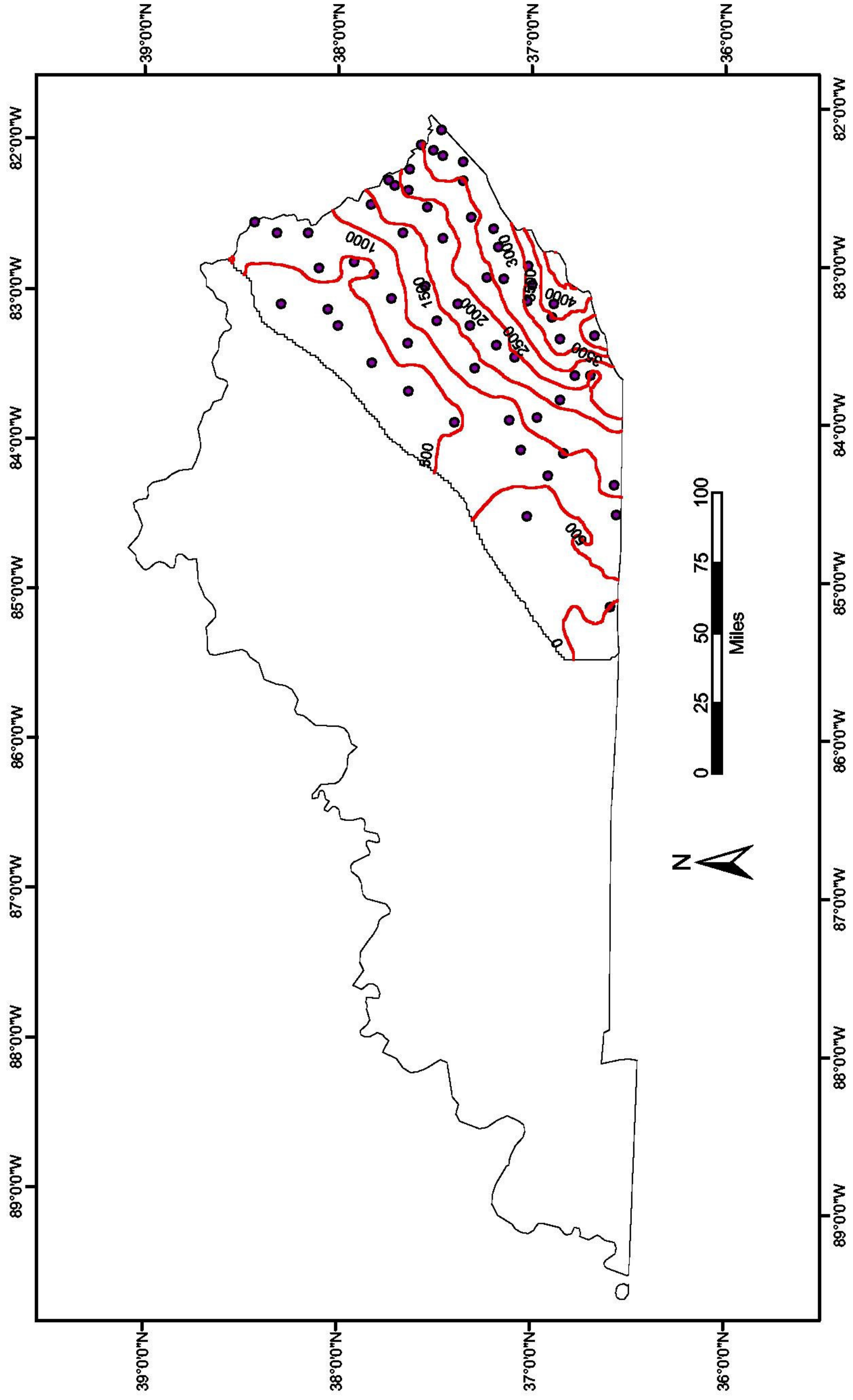


Figure M7. Contour map of depth to top of Unit 1 in Kentucky

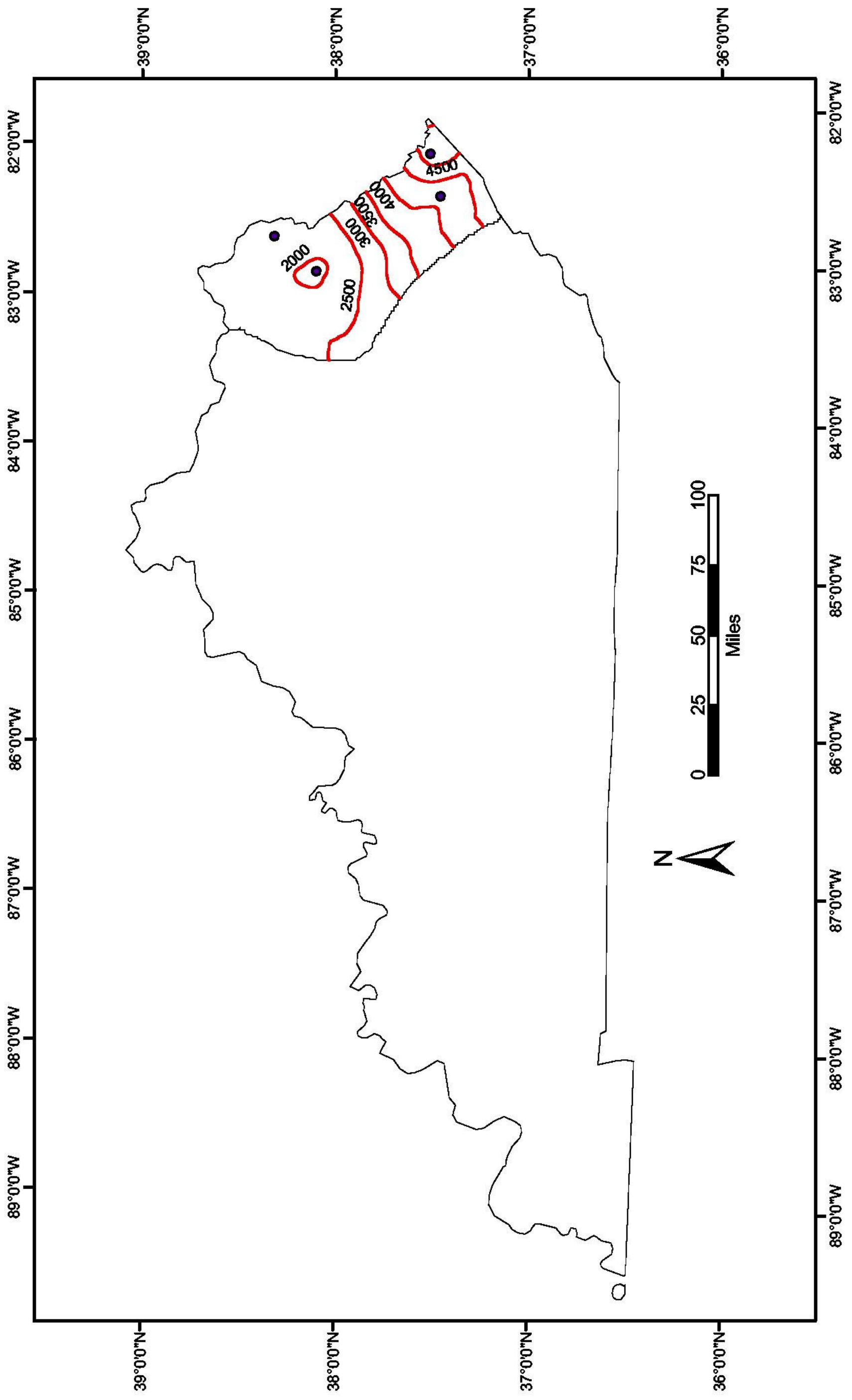


Figure M8. Contour map of depth to top of Unit 2/3 in Kentucky

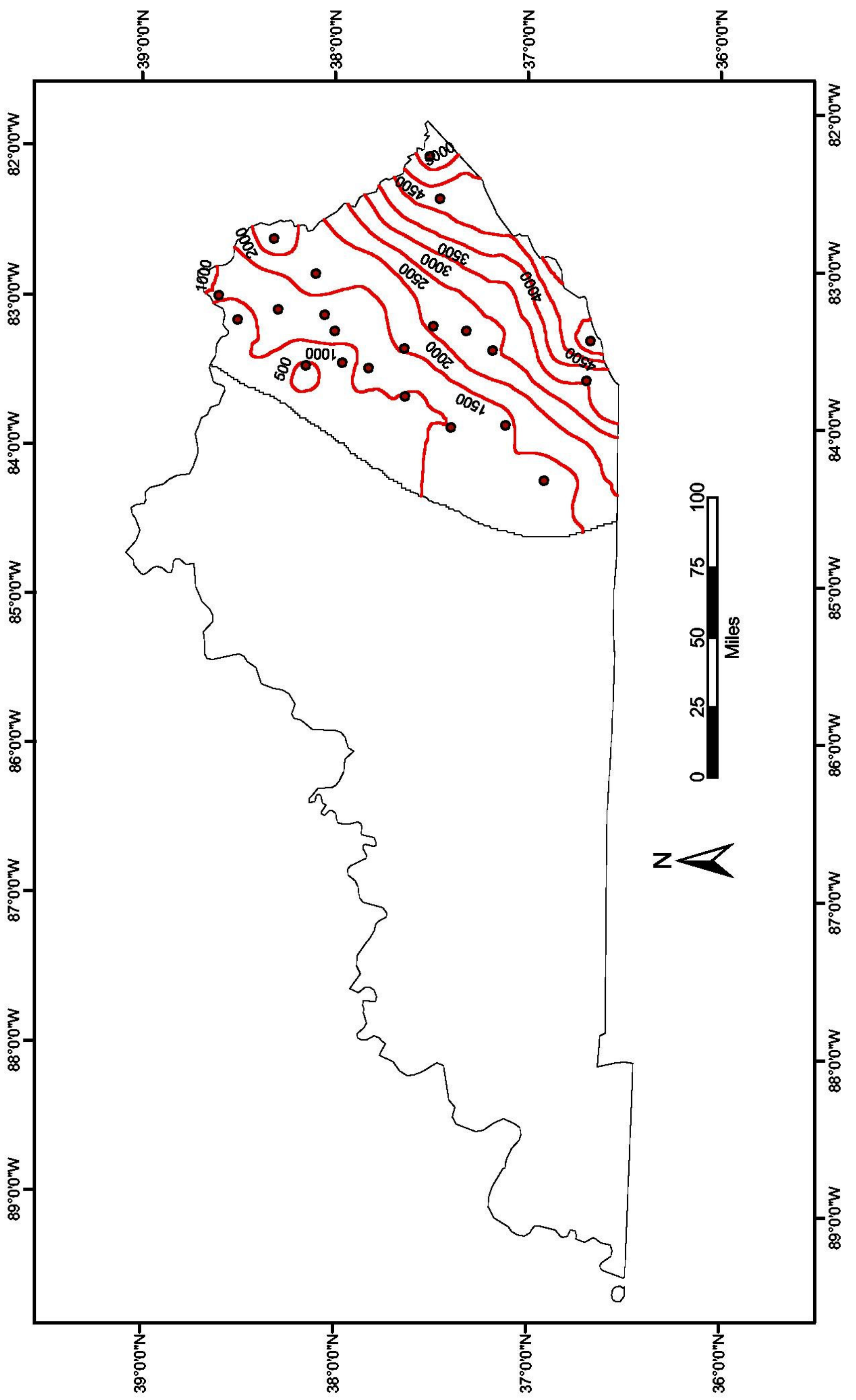


Figure M9. Contour map of depth to top of Unit 4 in Kentucky

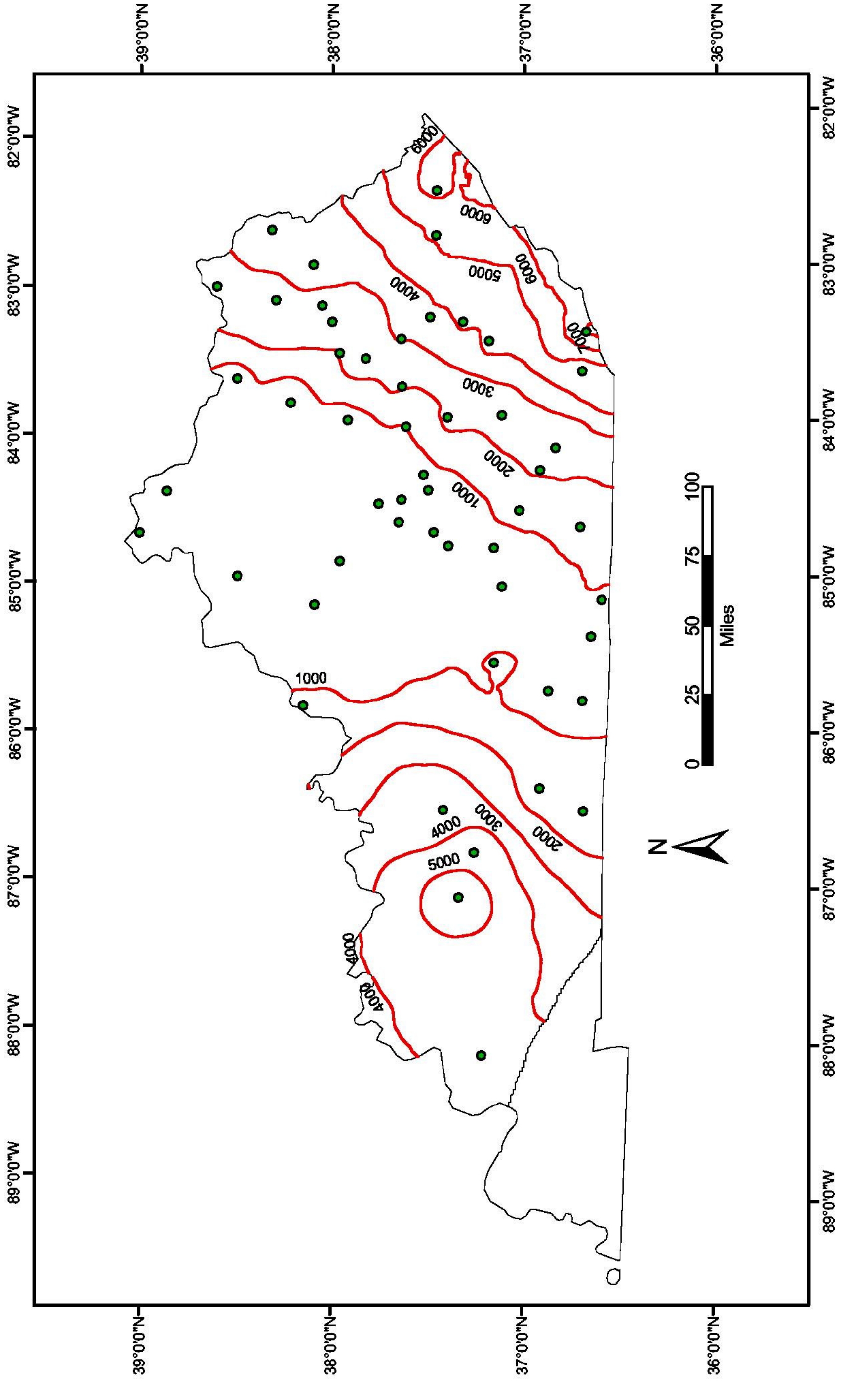


Figure M10. Contour map of depth to top of Unit 5 in Kentucky

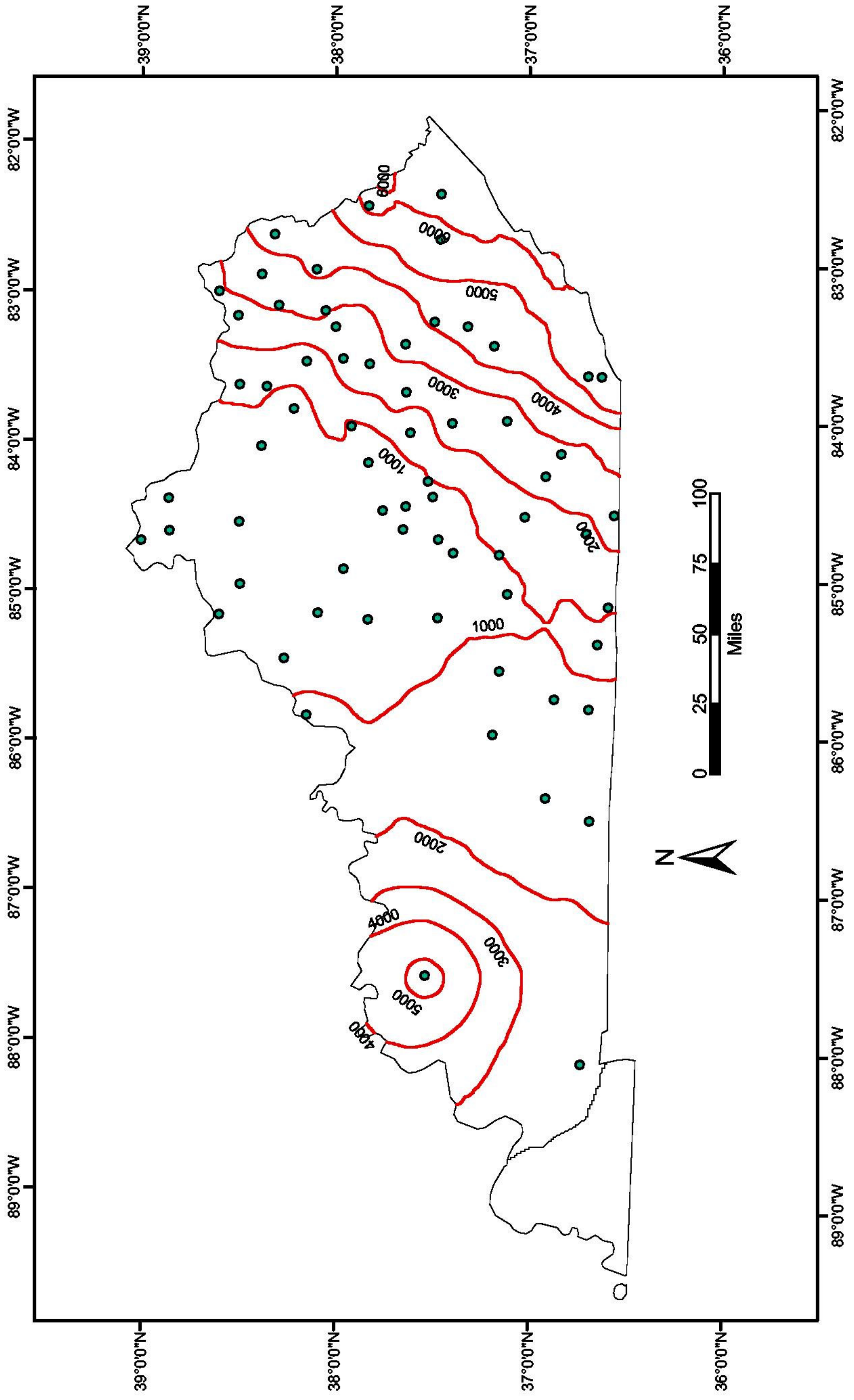


Figure M11. Contour map of depth to top of Unit 6 in Kentucky

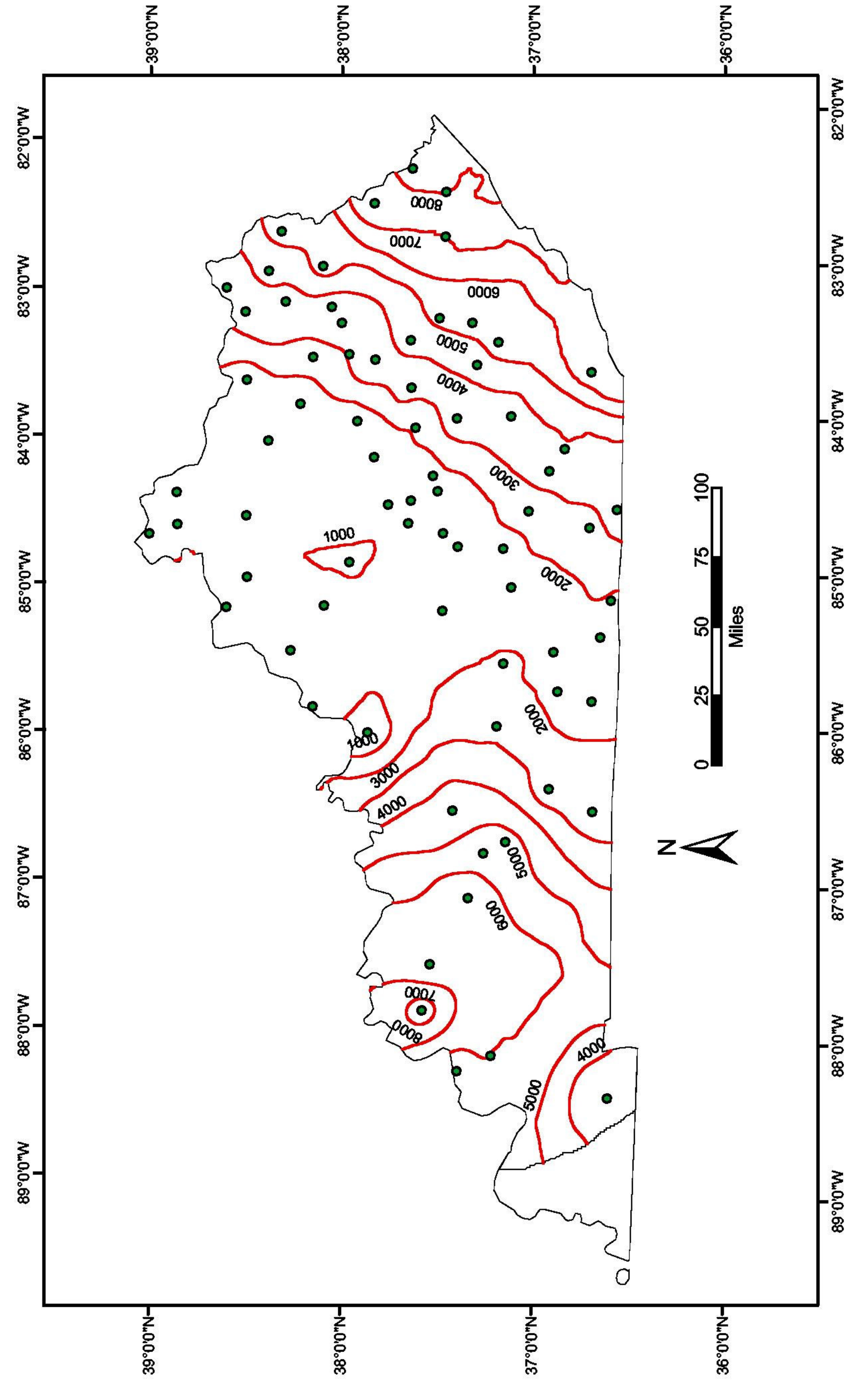


Figure M12. Contour map of depth to top of Unit 7 in Kentucky

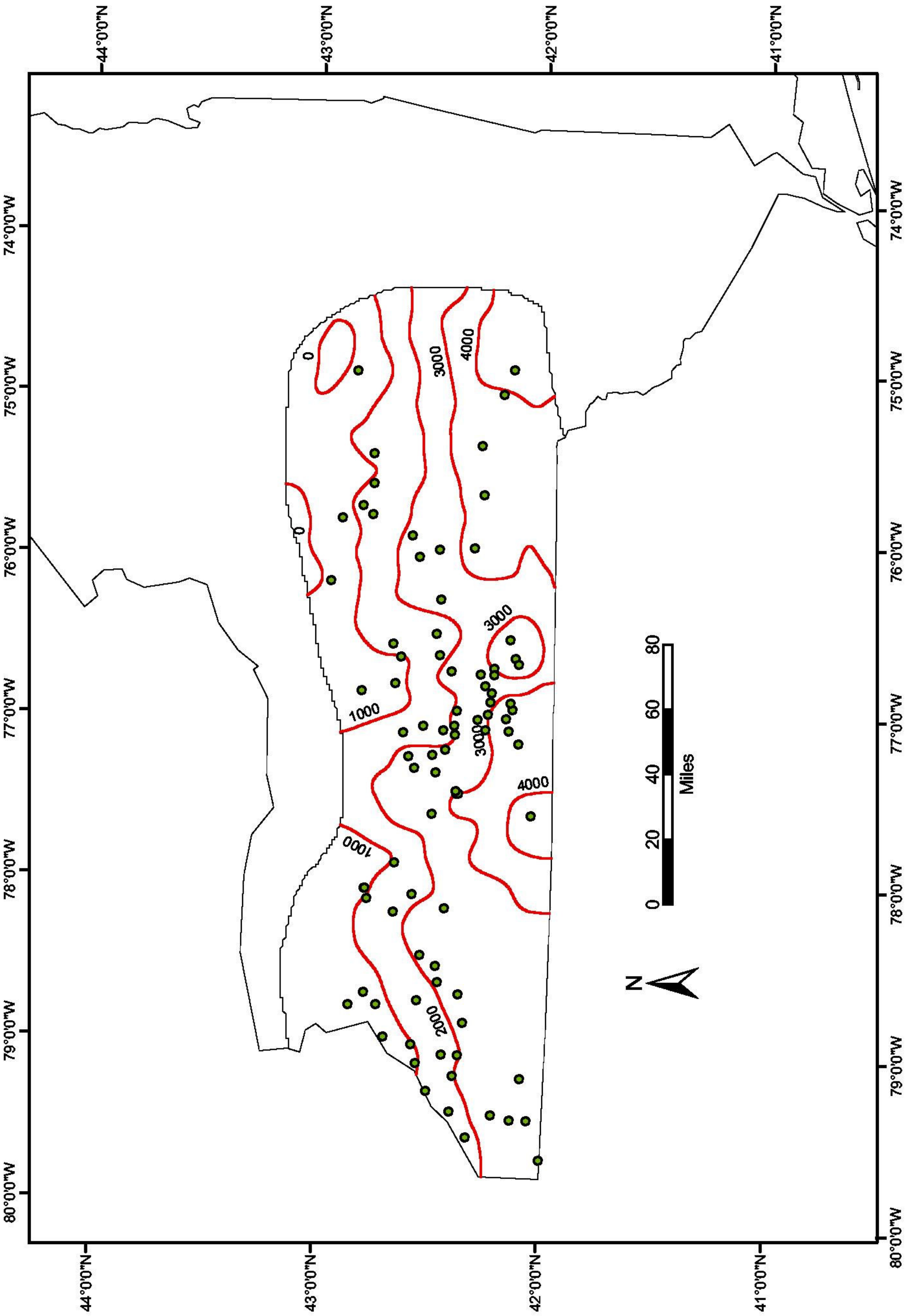


Figure M13. Contour map of depth to top of Unit 2 in New York

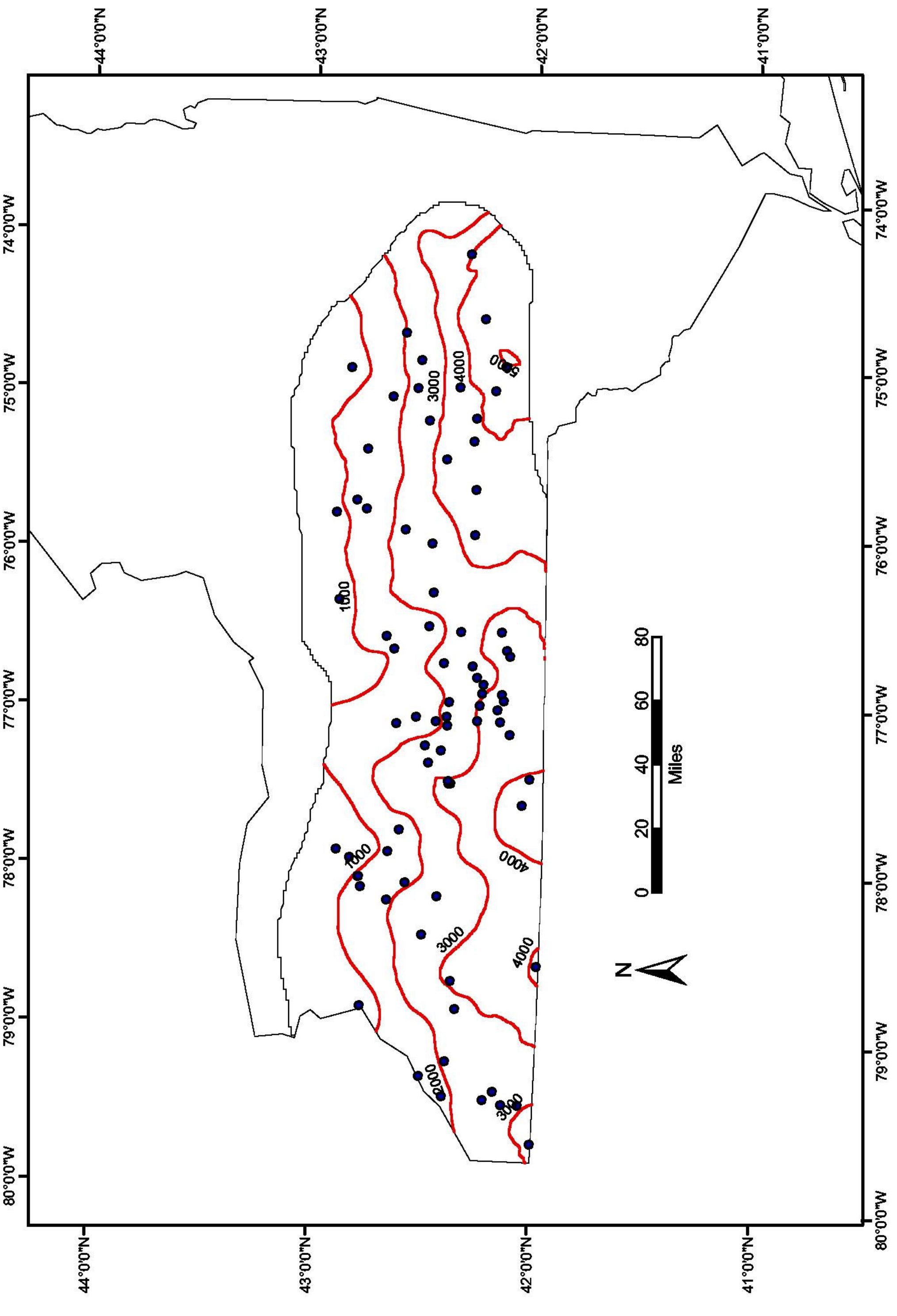


Figure M14. Contour map of depth to top of Unit 3 in New York

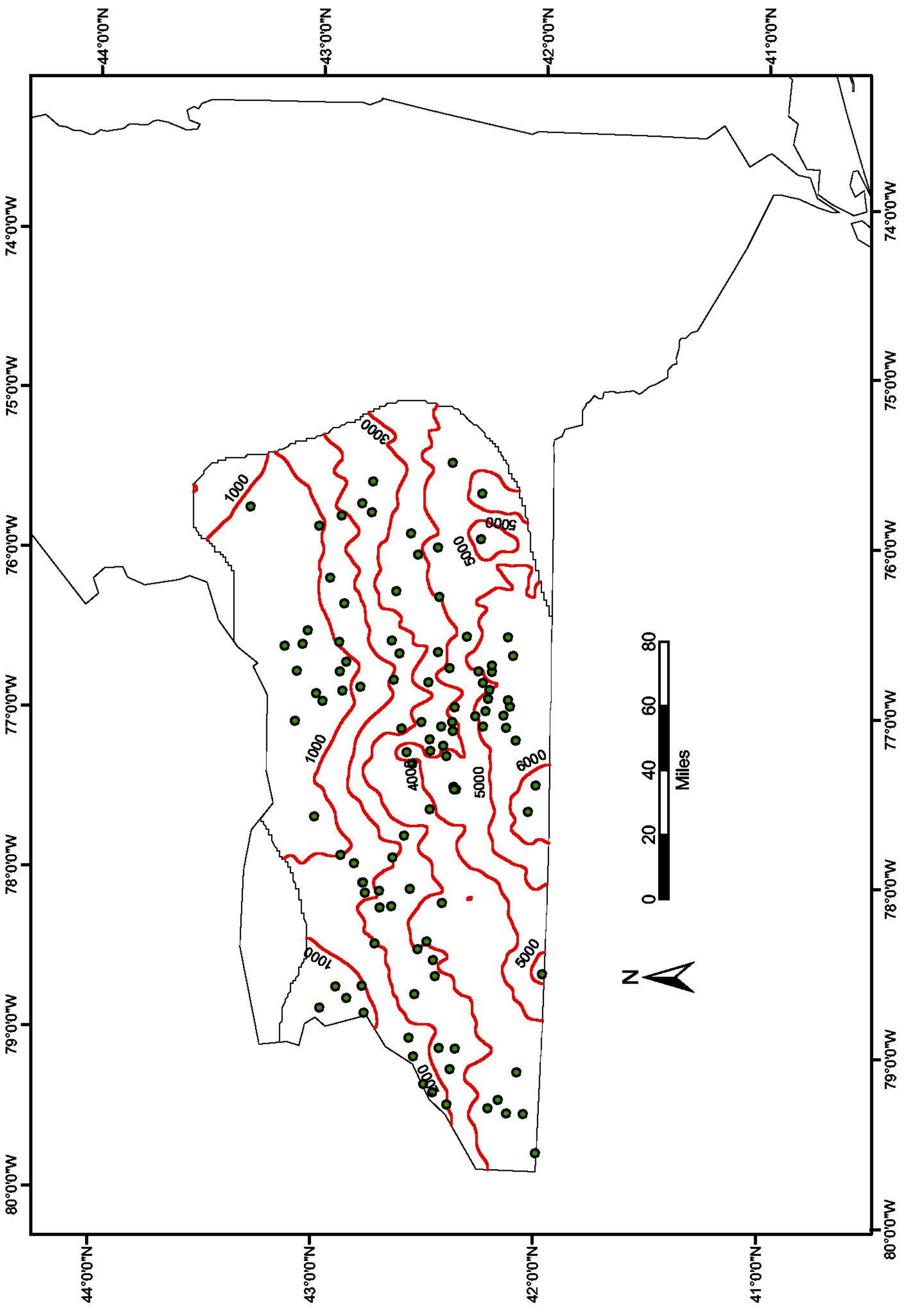


Figure M15. Contour map of depth to top of Unit 4 in New York

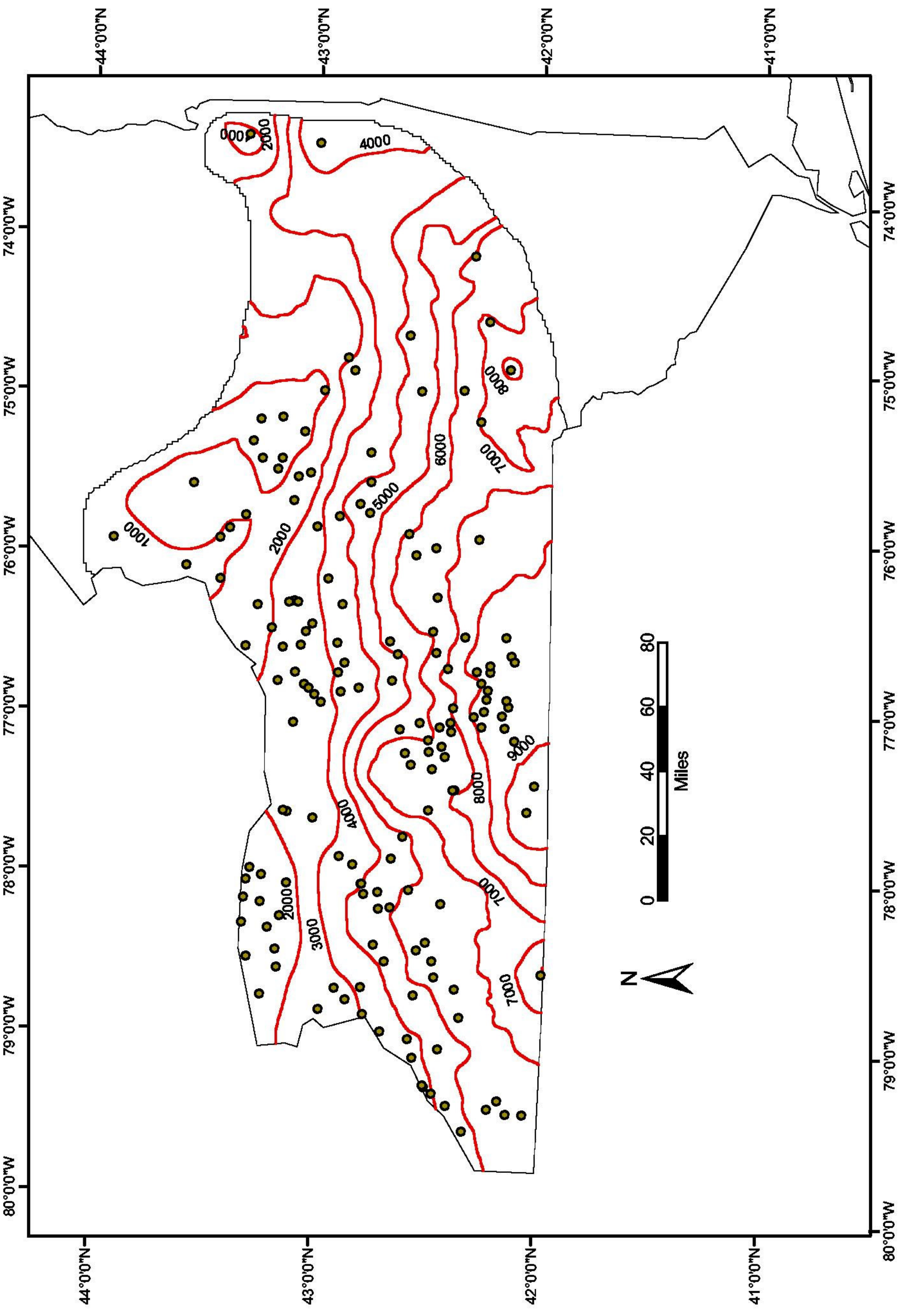


Figure M16. Contour map of depth to top of Unit 5 in New York

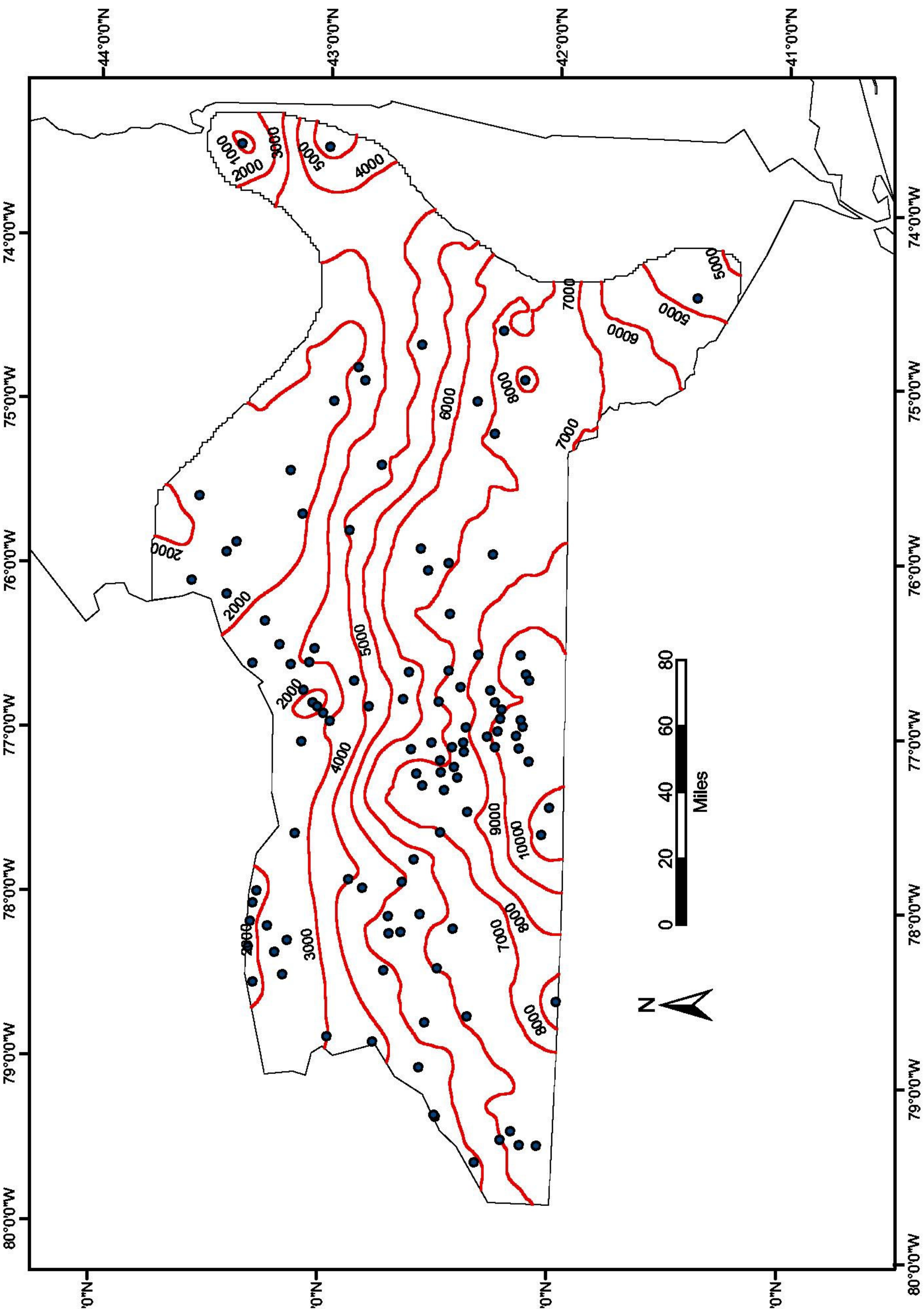
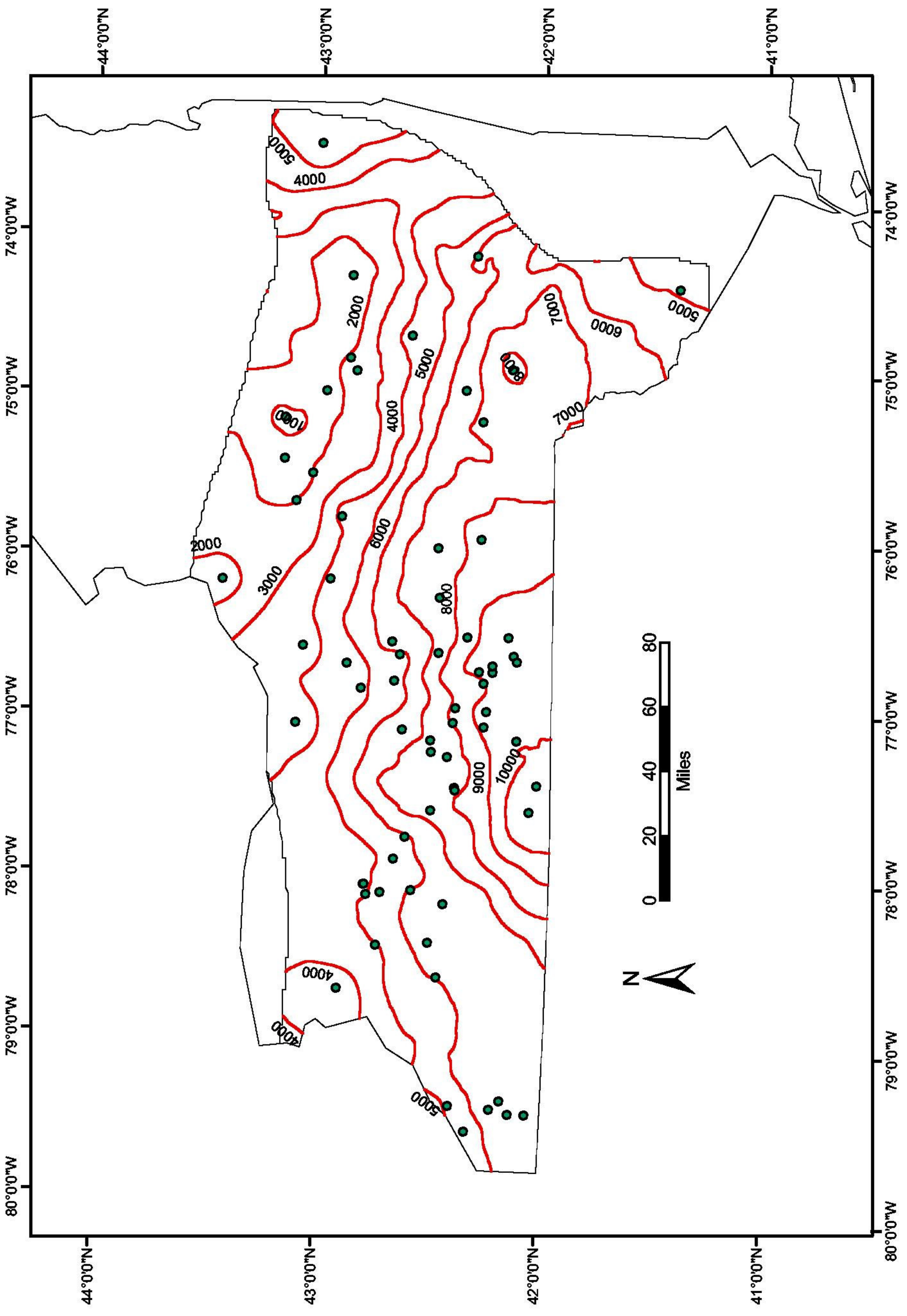


Figure M17. Contour map of depth to top of Unit 6 in New York



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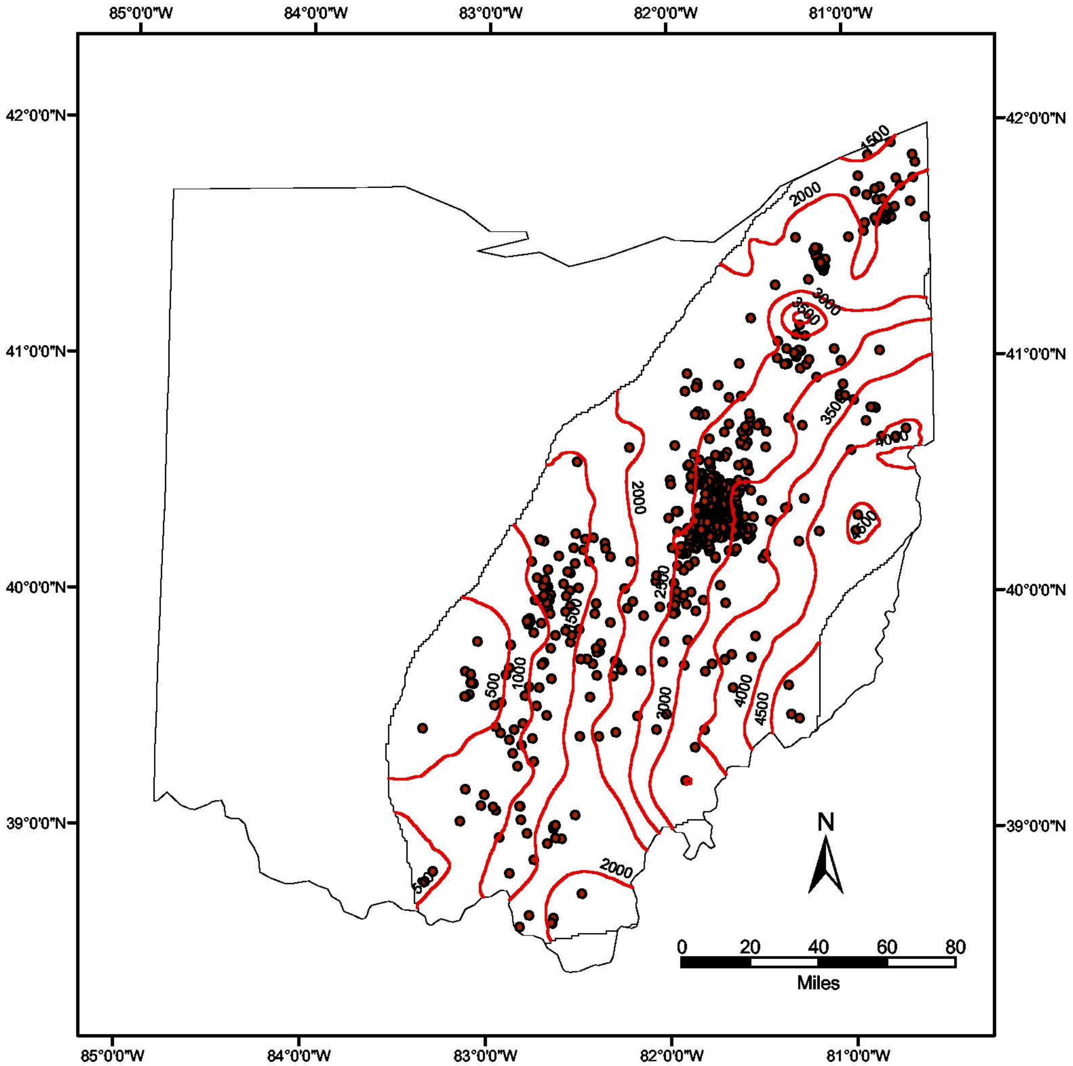


Figure M19. Contour map of depth to top of Unit 2 in Ohio

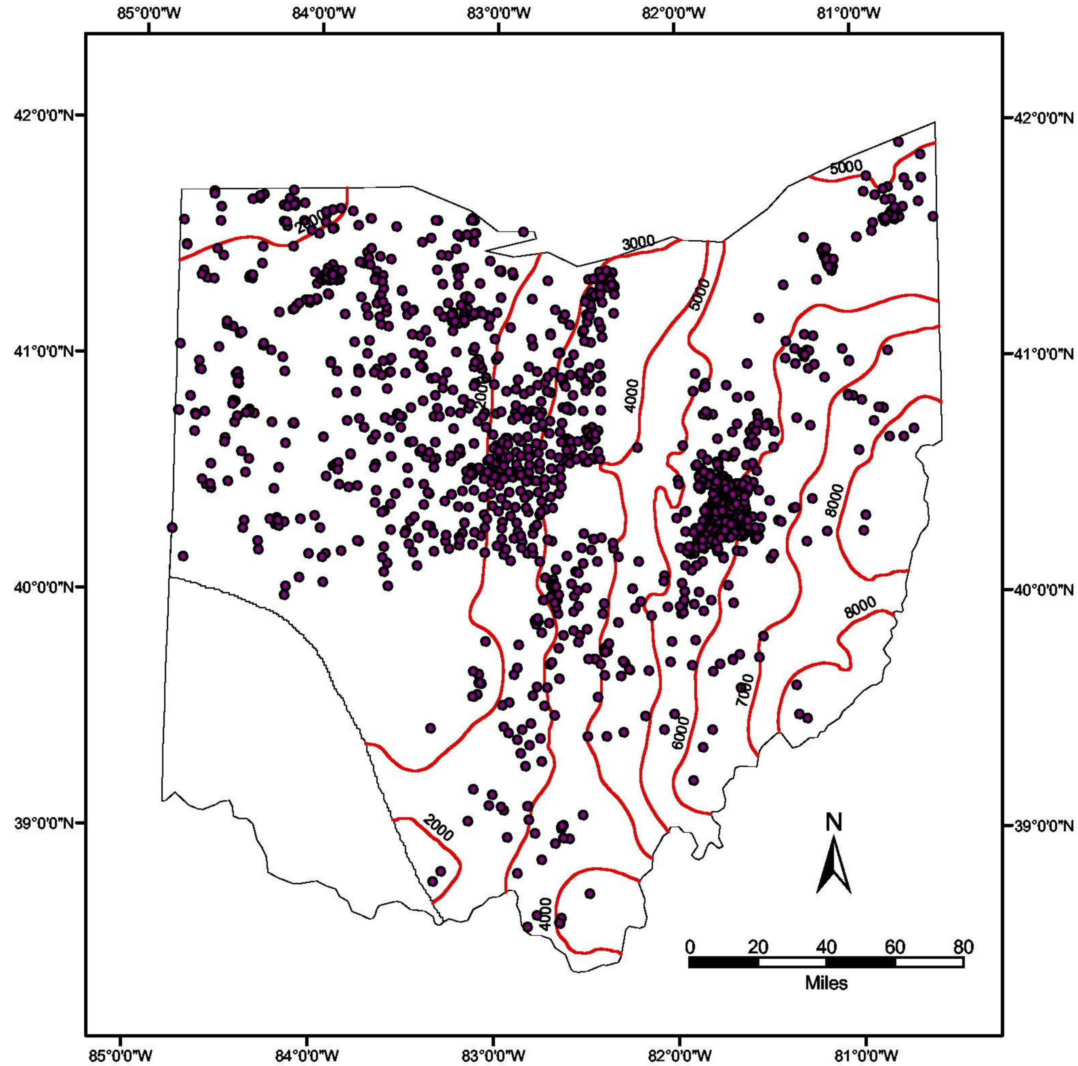


Figure M20. Contour map of depth to top of Unit 5 in Ohio

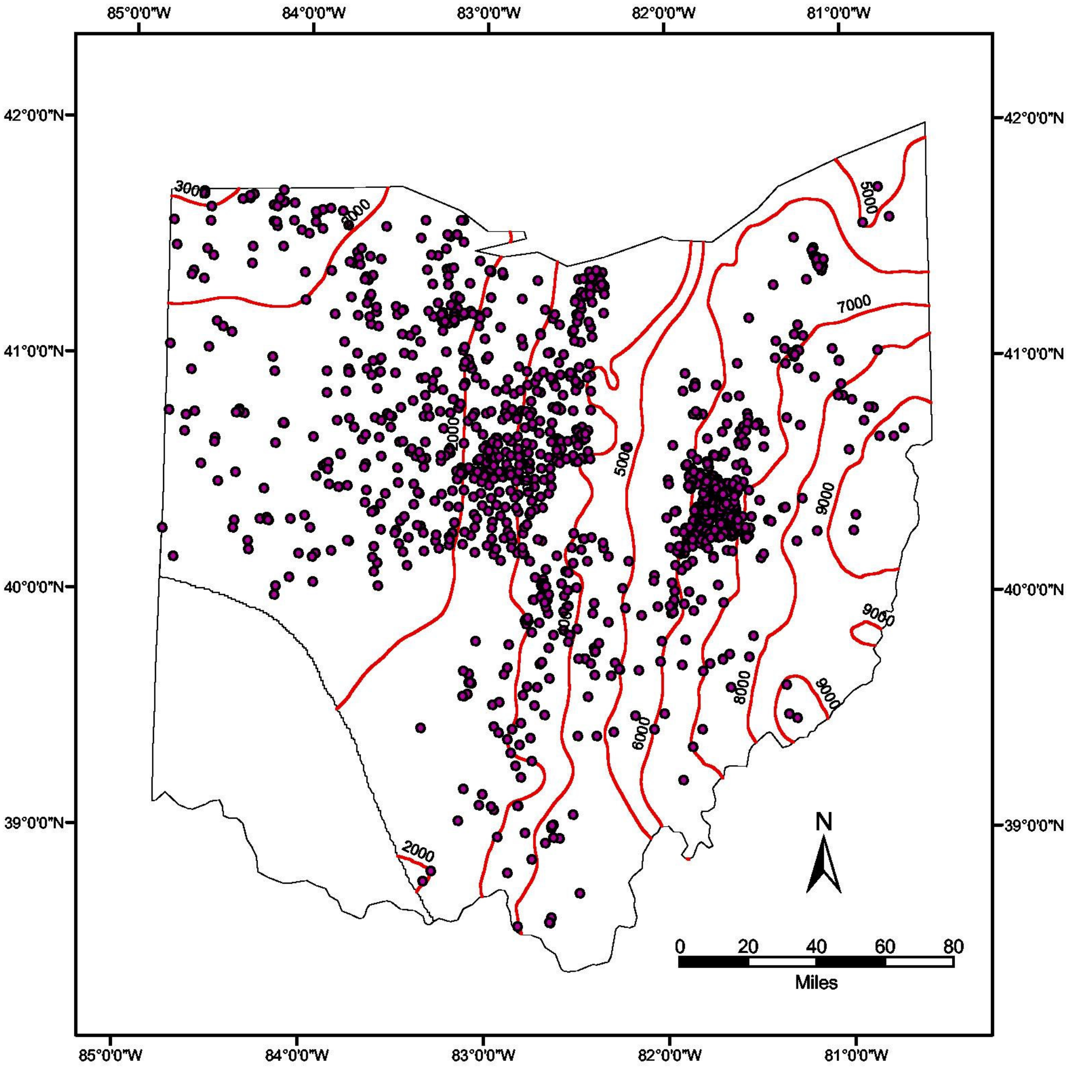
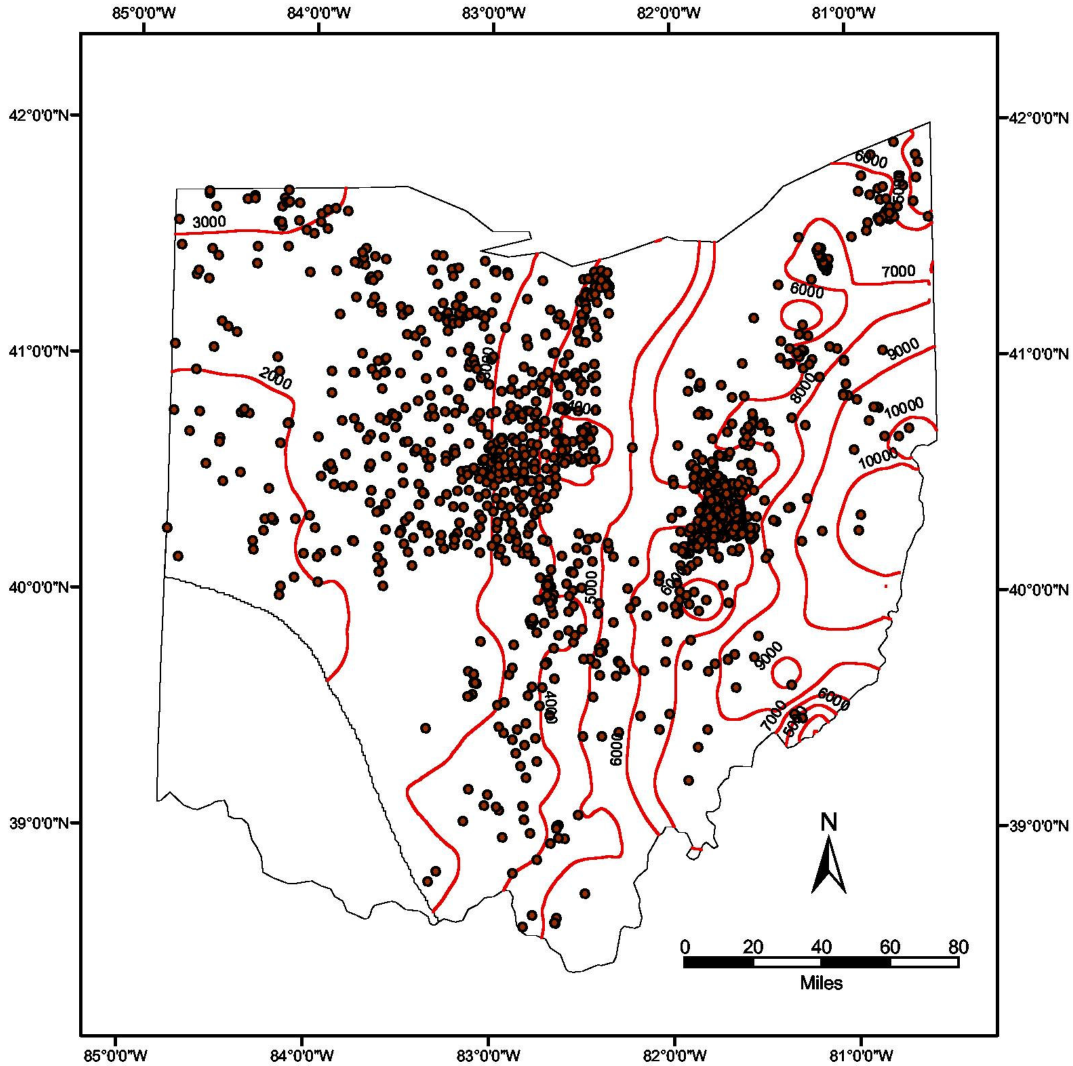


Figure M21. Contour map of depth to top of Unit 6 in Ohio



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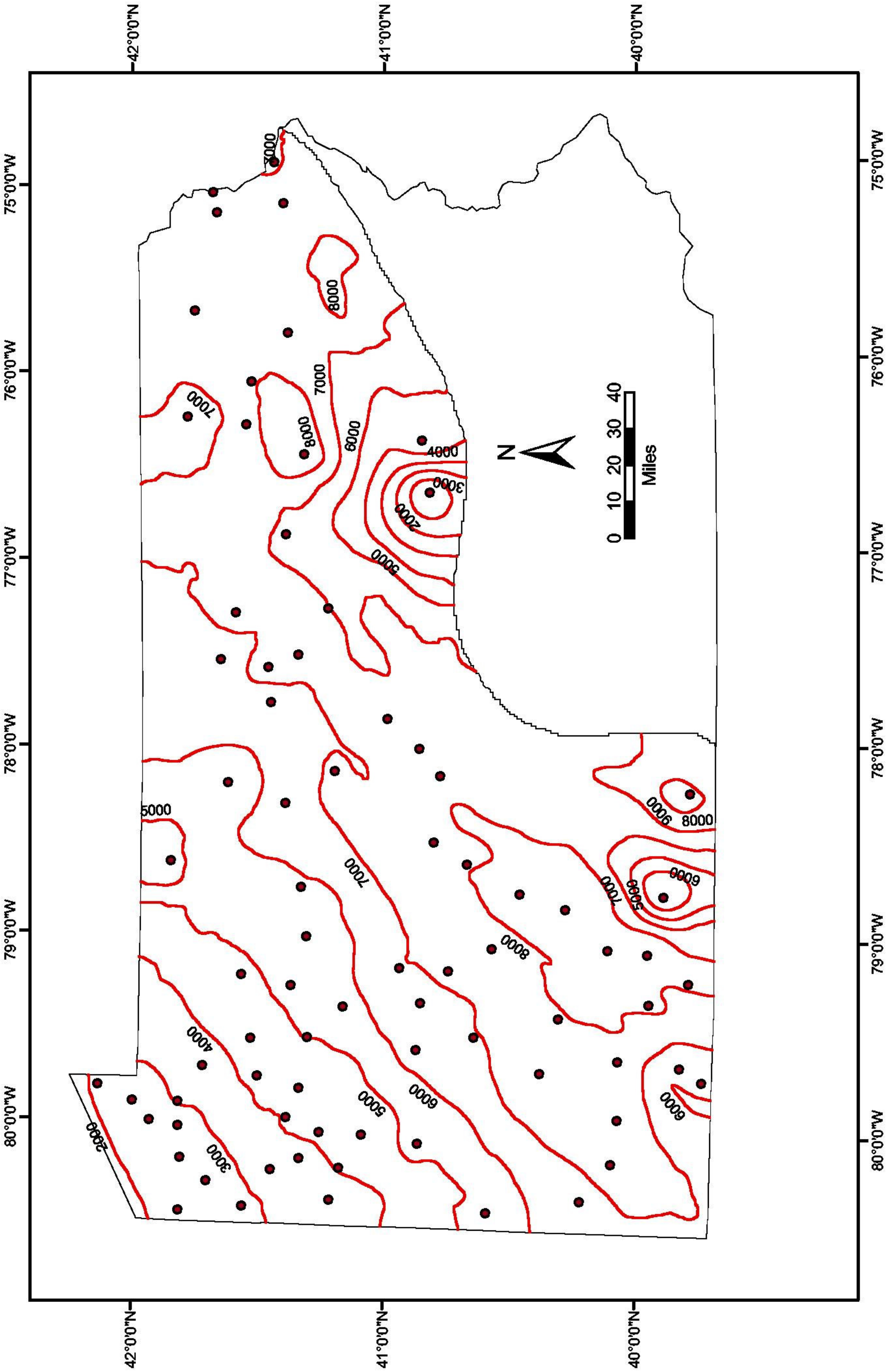
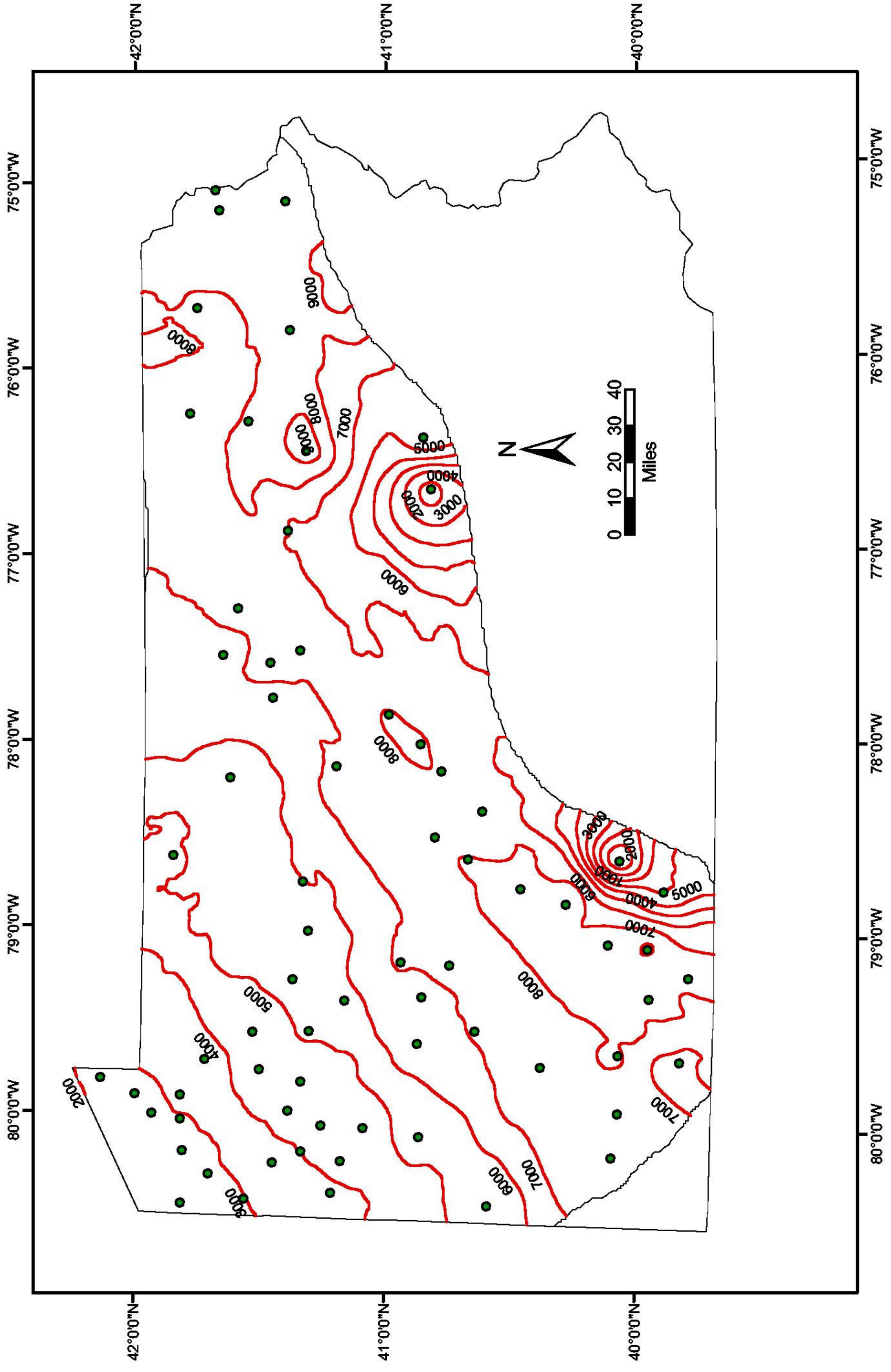


Figure M23. Contour map of depth to top of Unit 2 in Pennsylvania



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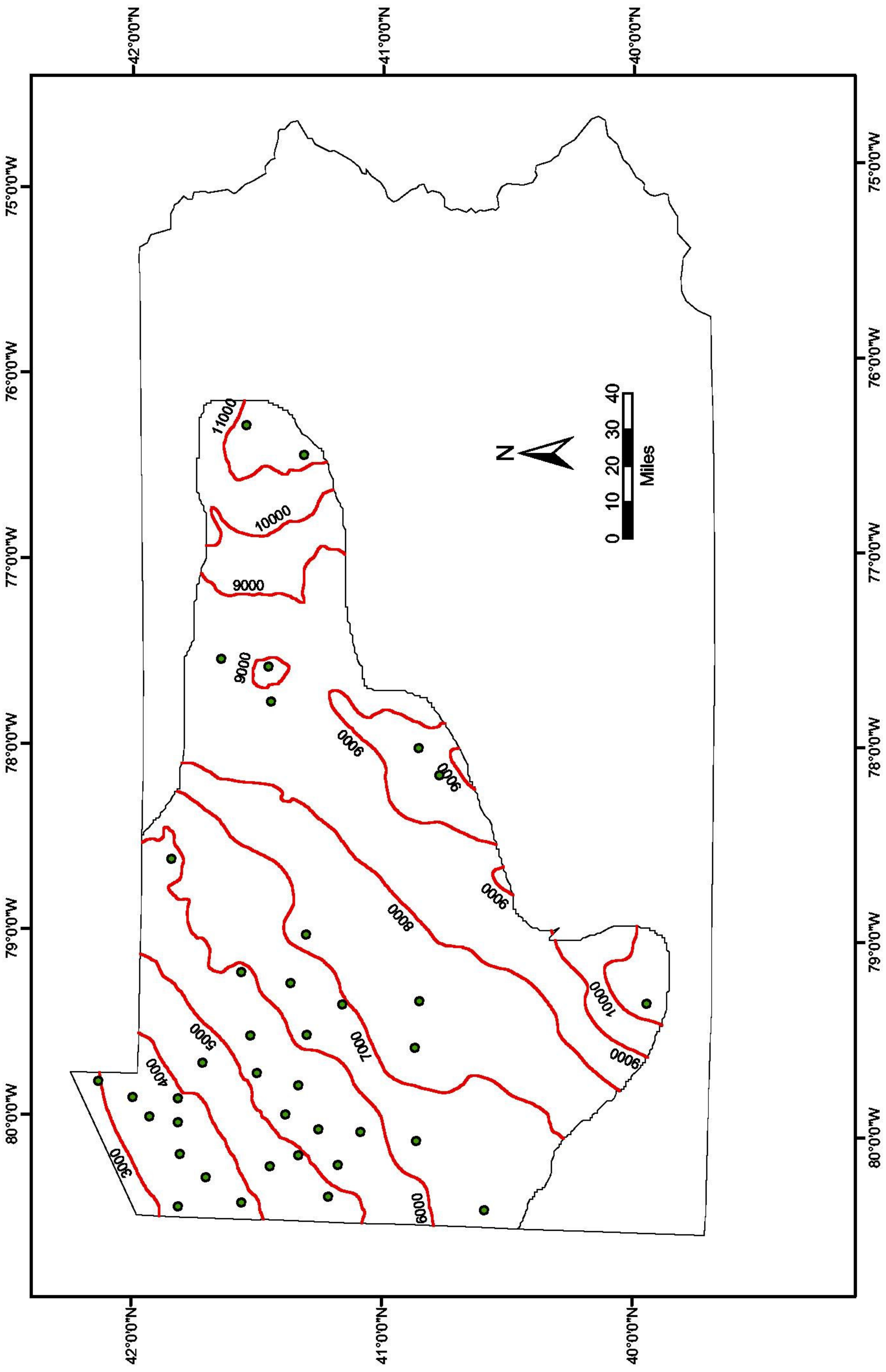

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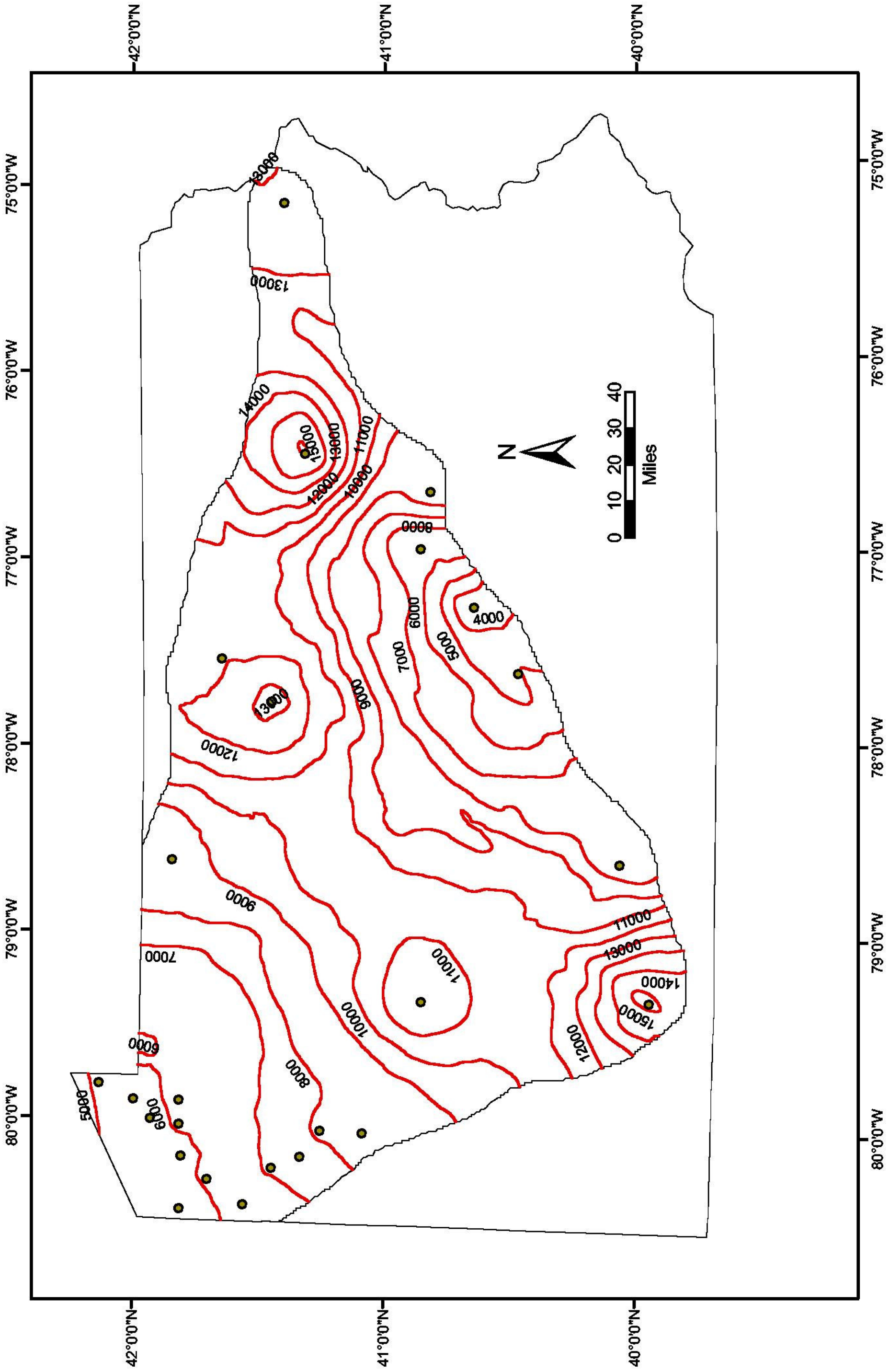

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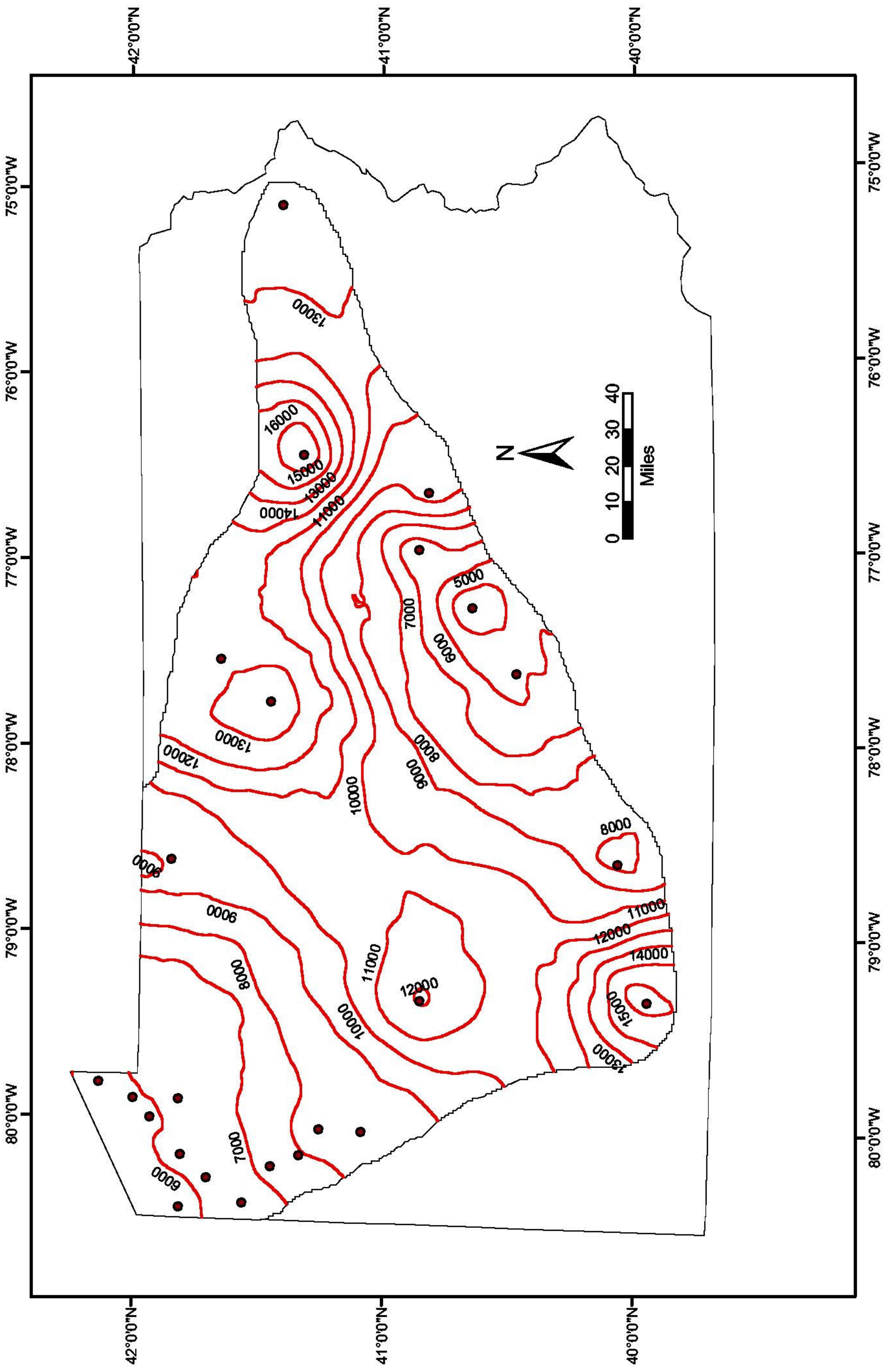

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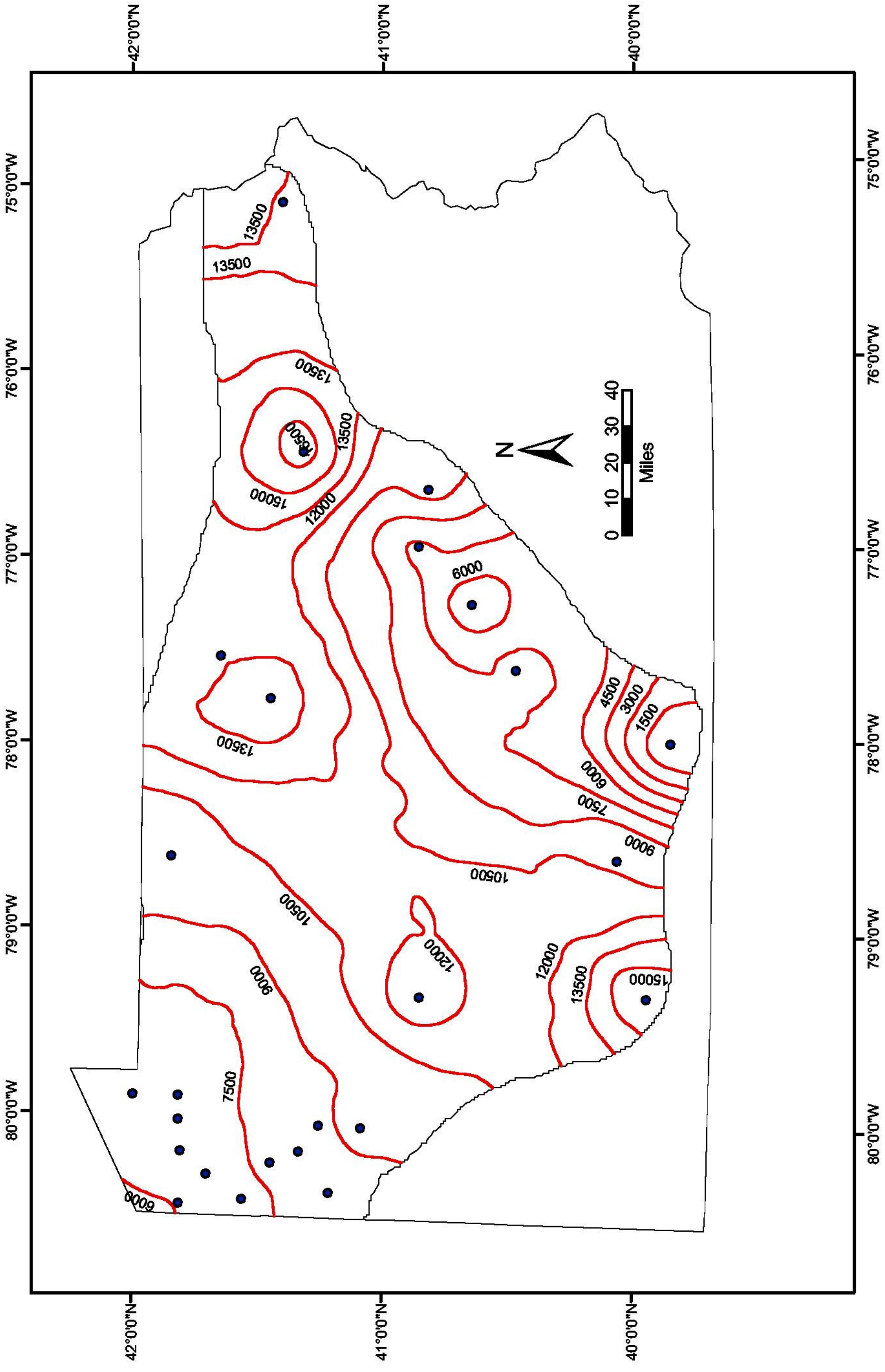

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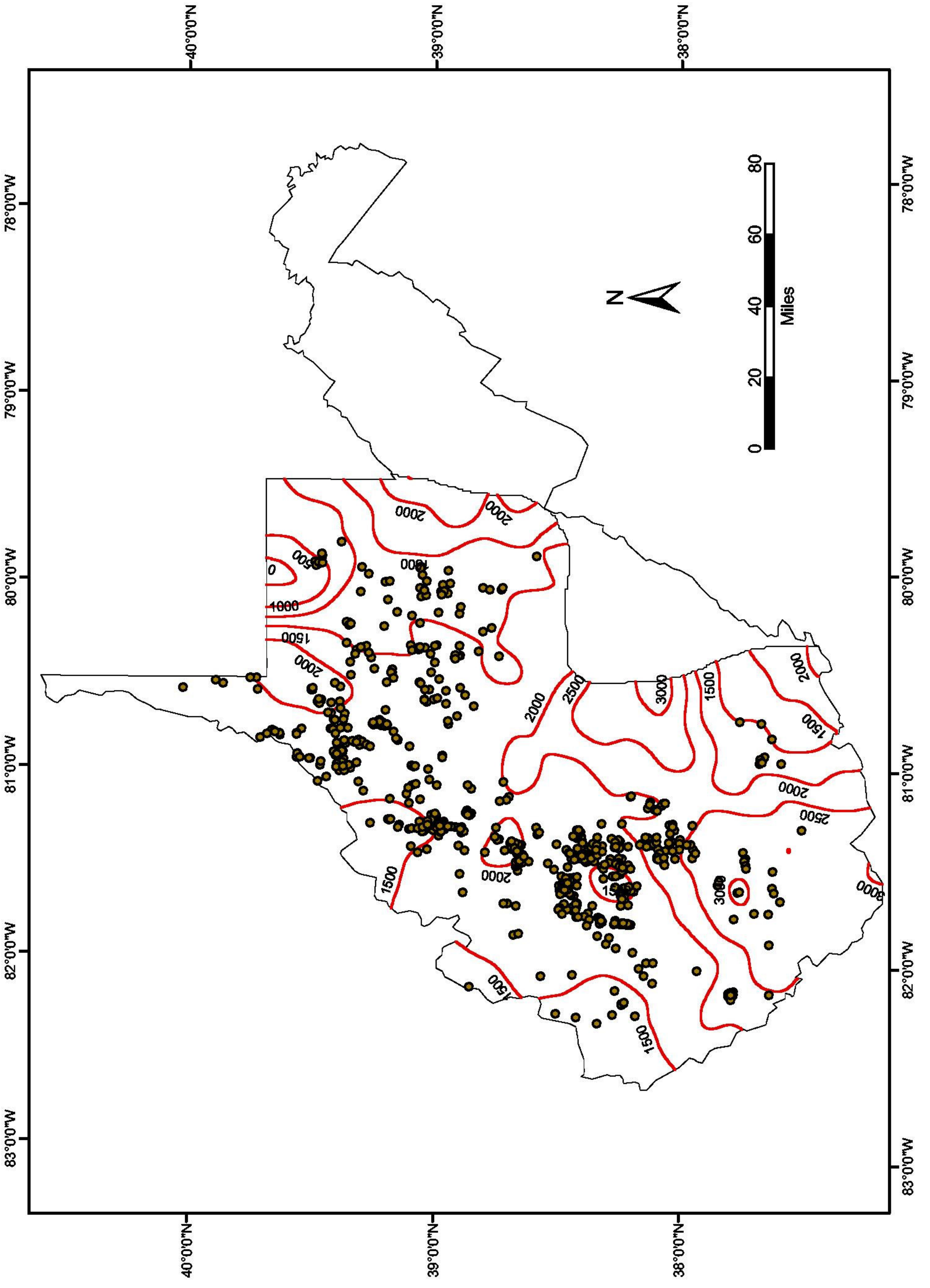

Figure M29. Contour map of depth to top of Unit 1 in West Virginia

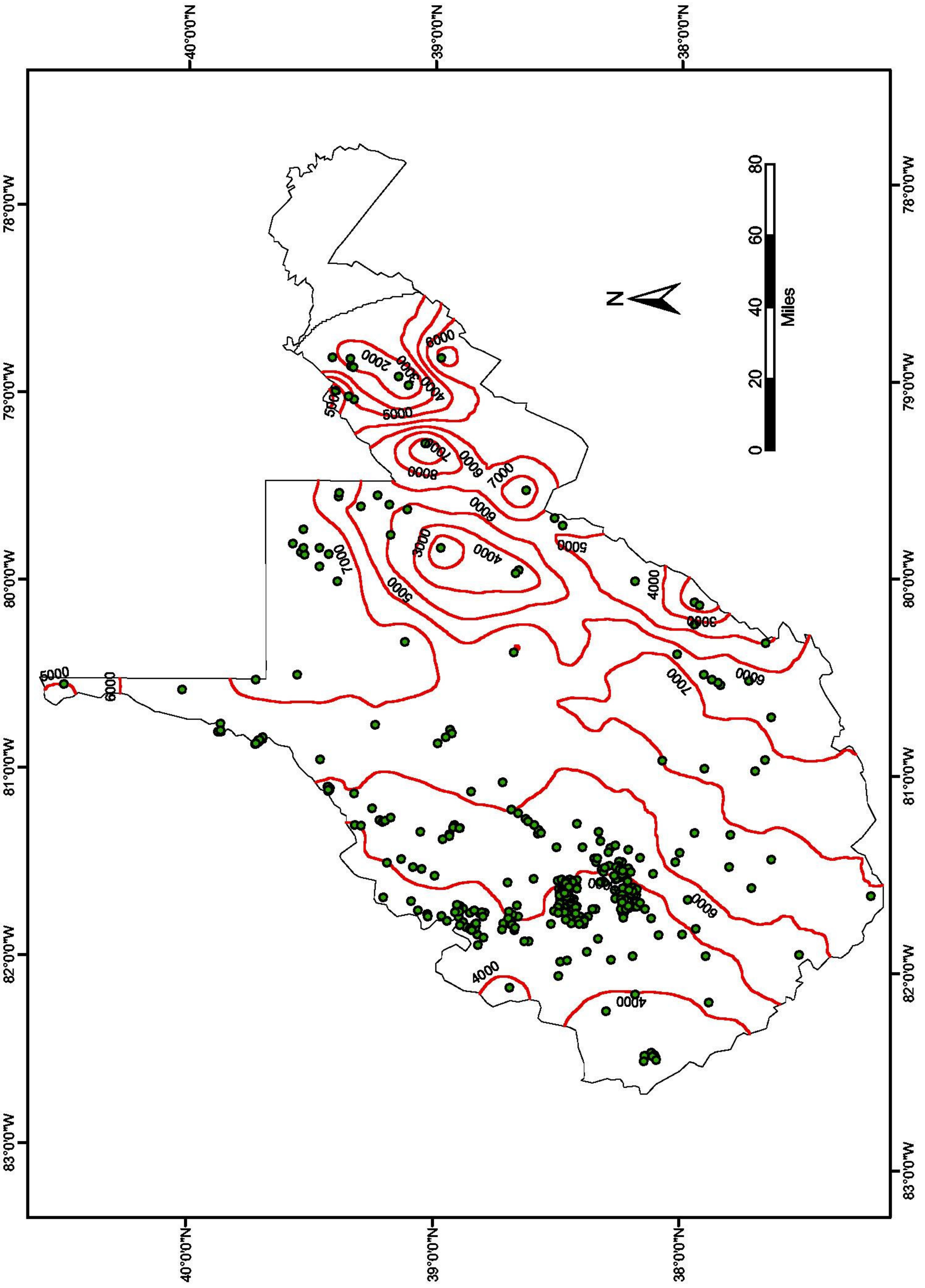

Figure M30. Contour map of depth to top of Subunit 3a in West Virginia

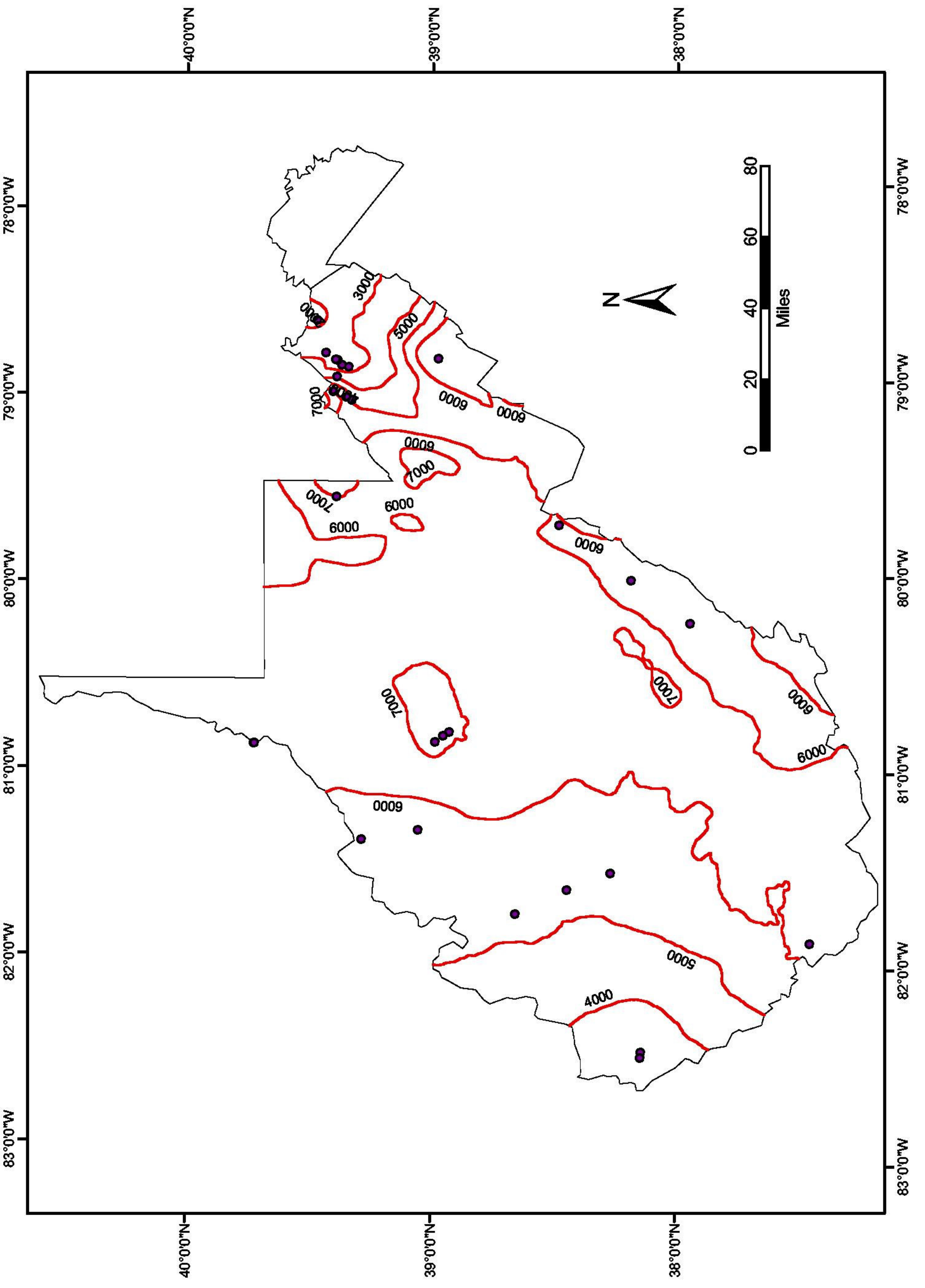

Figure M31. Contour map of depth to top of Subunit 3b in West Virginia

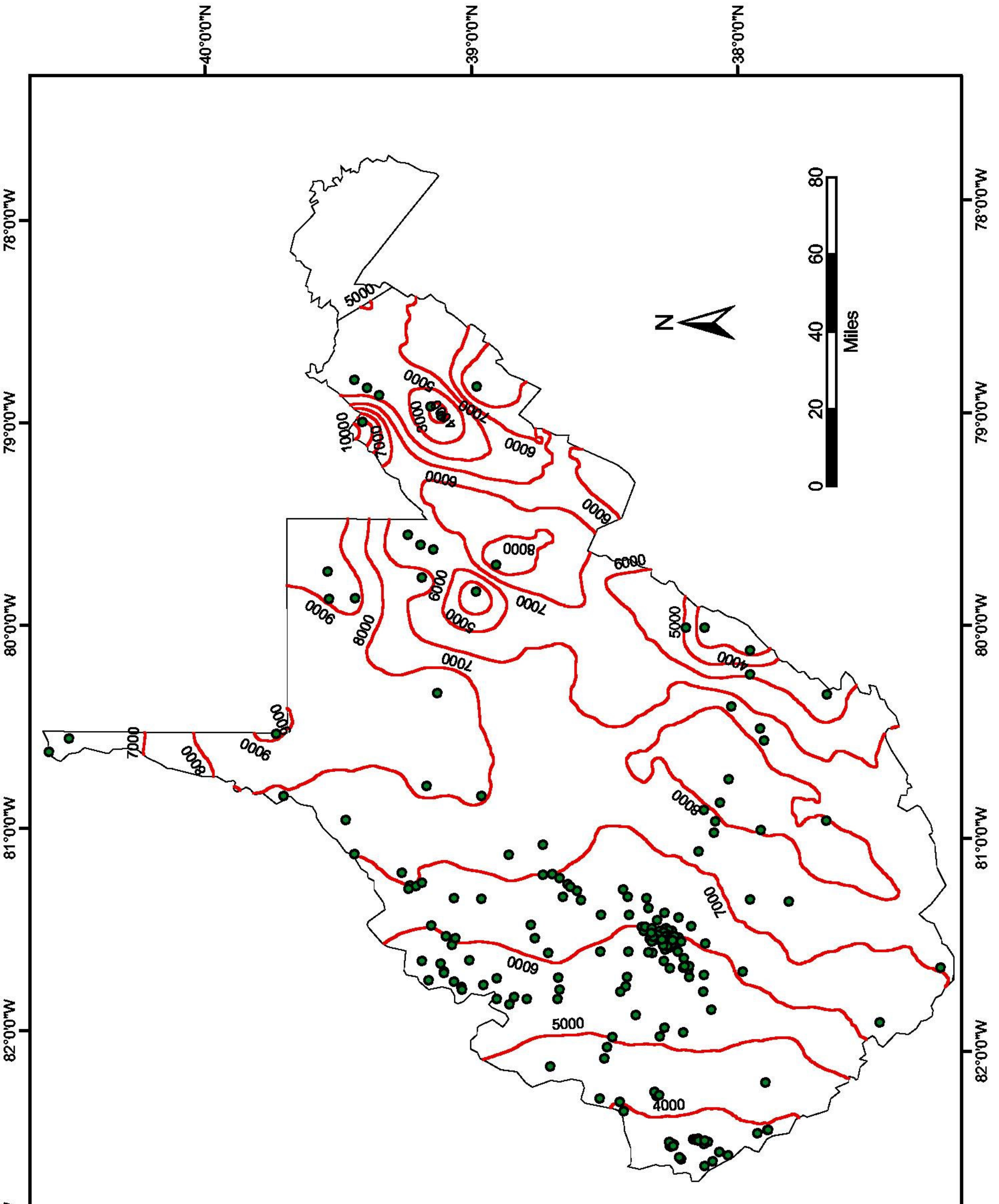

Figure M32. Contour map of depth to top of Unit 4 in West Virginia

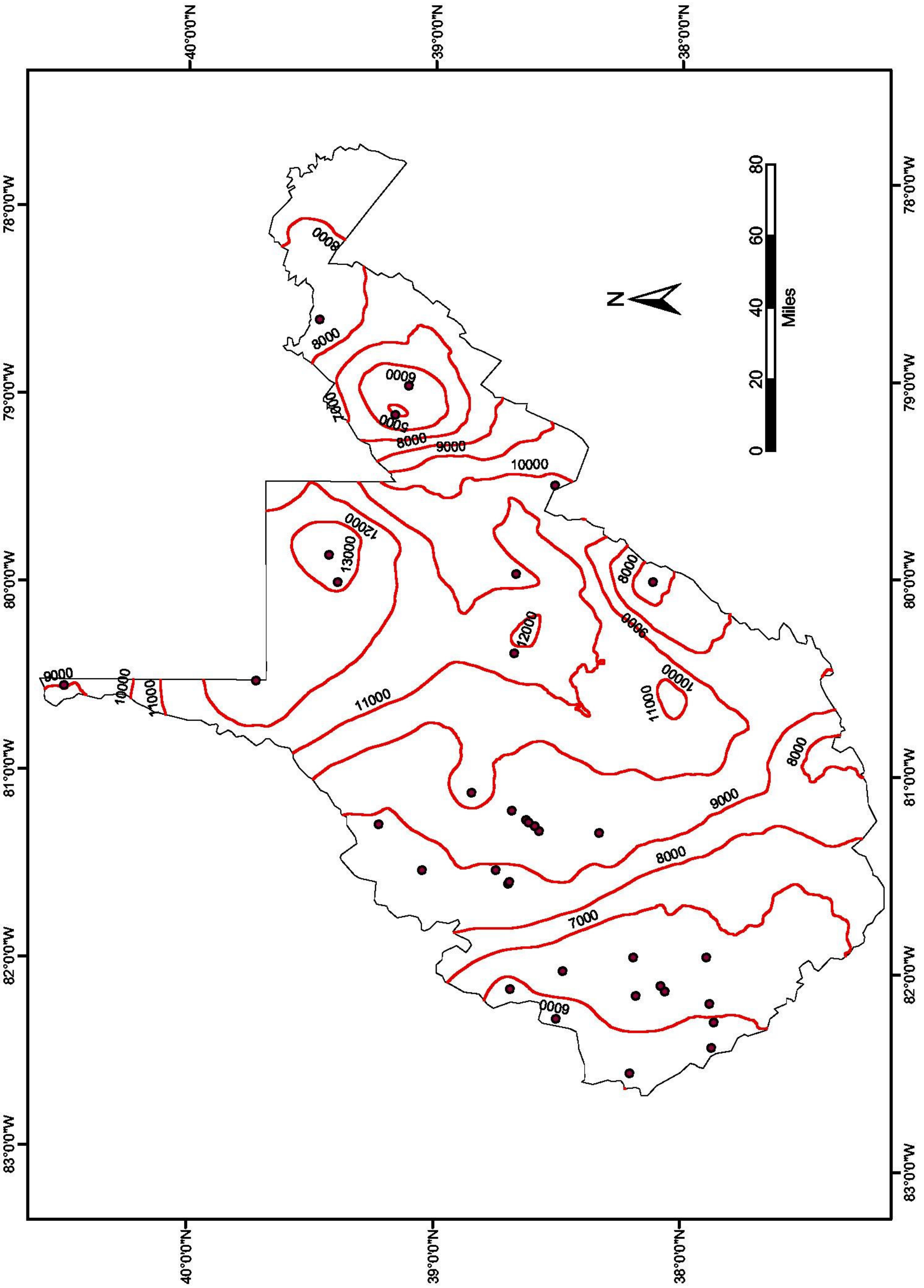

Figure M33. Contour map of depth to top of Unit 5 in West Virginia

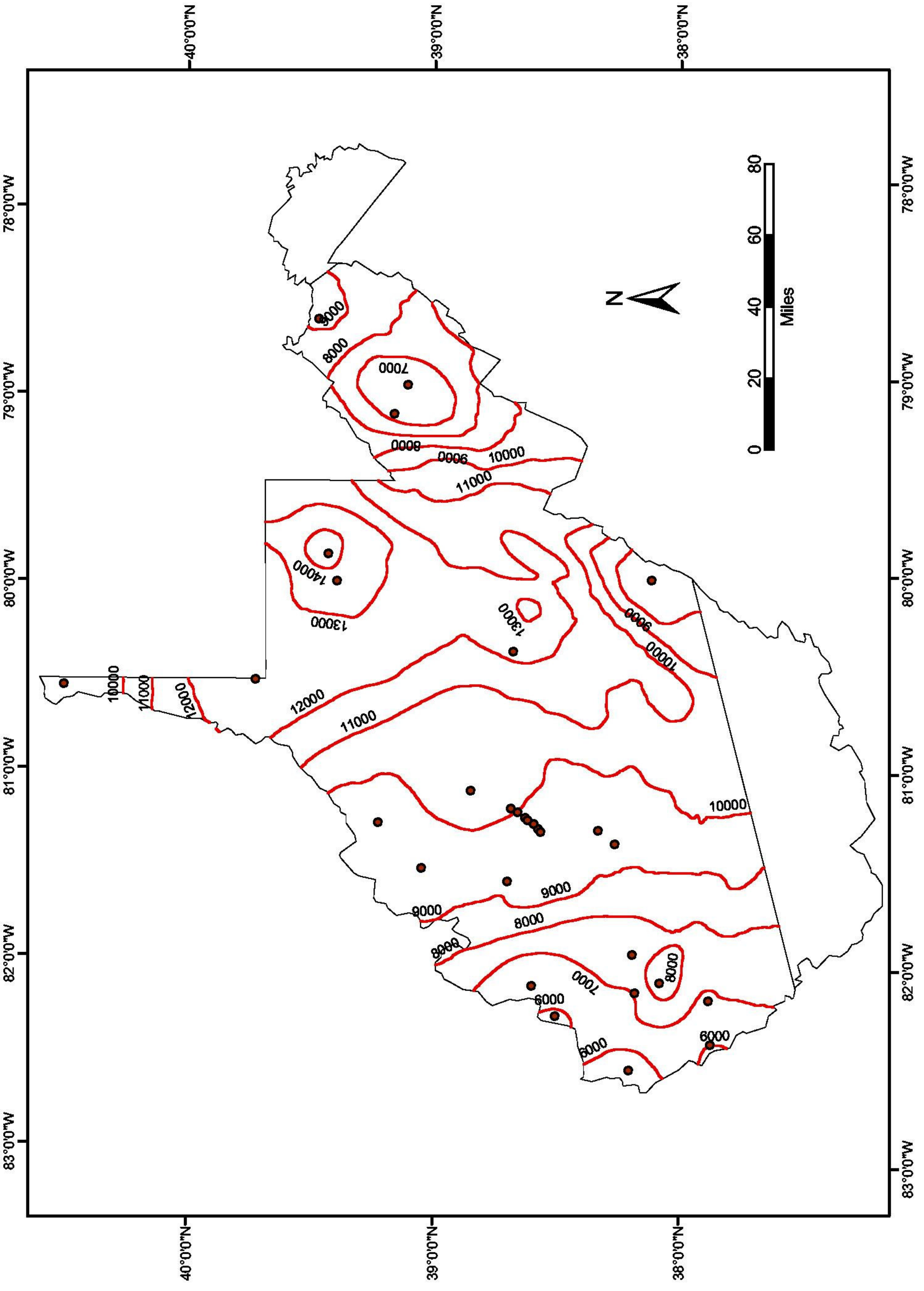

Figure M34. Contour map of depth to top of Unit 6 in West Virginia

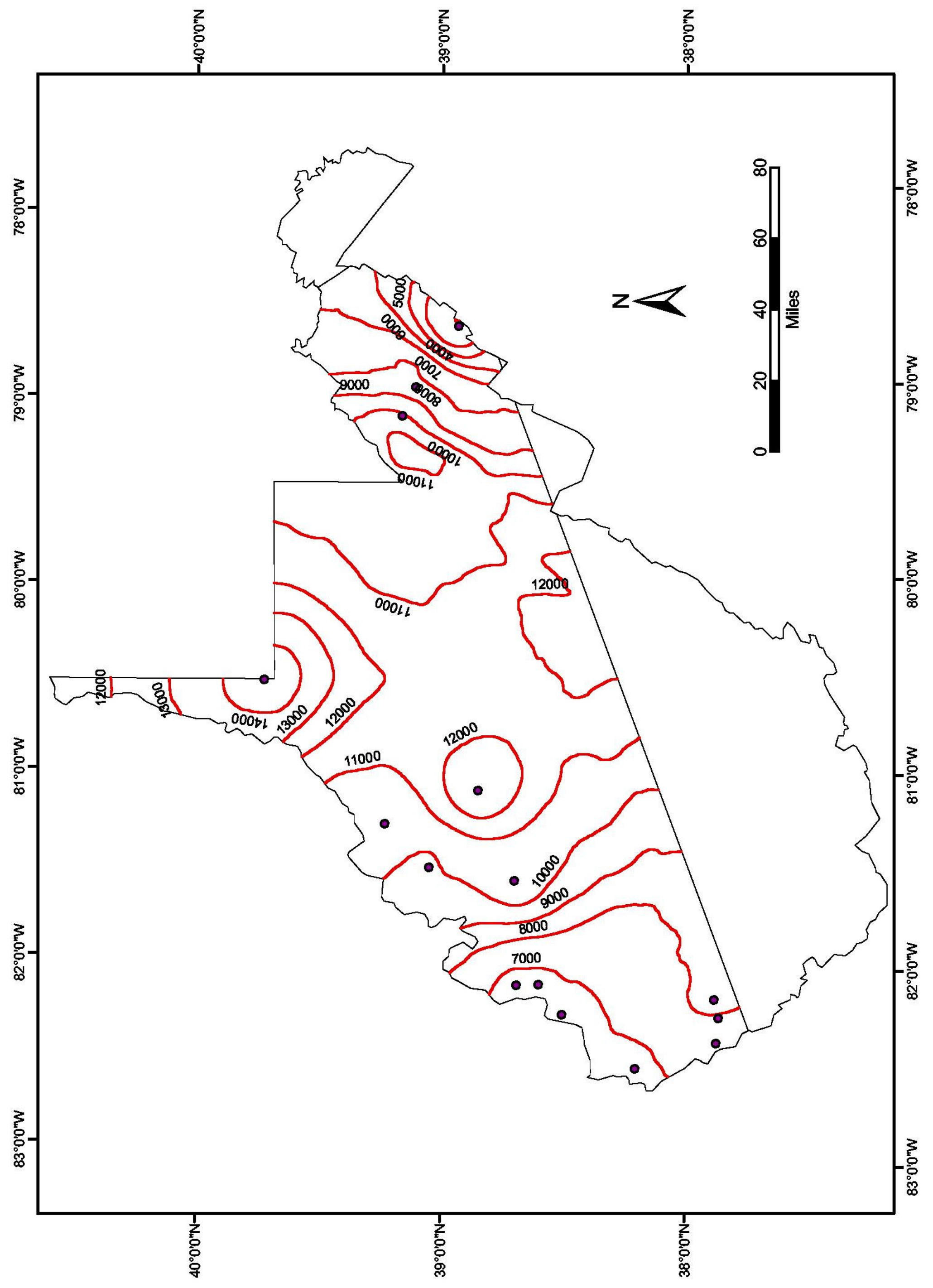

Figure M35. Contour map of depth to top of Unit 7 in West Virginia

Unit Thickness Maps

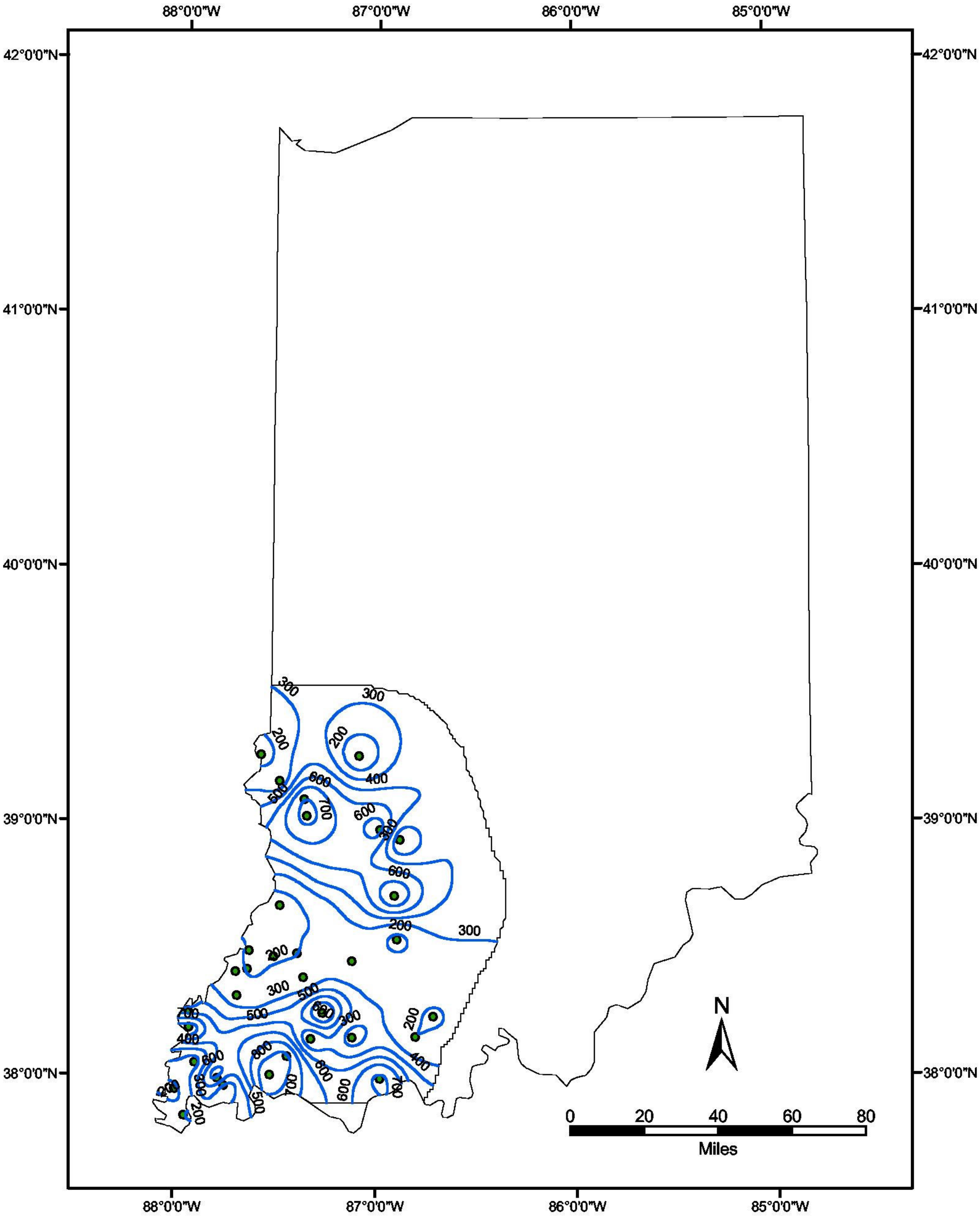

Figure M36. Contour map of thickness of Unit 1 in Indiana.

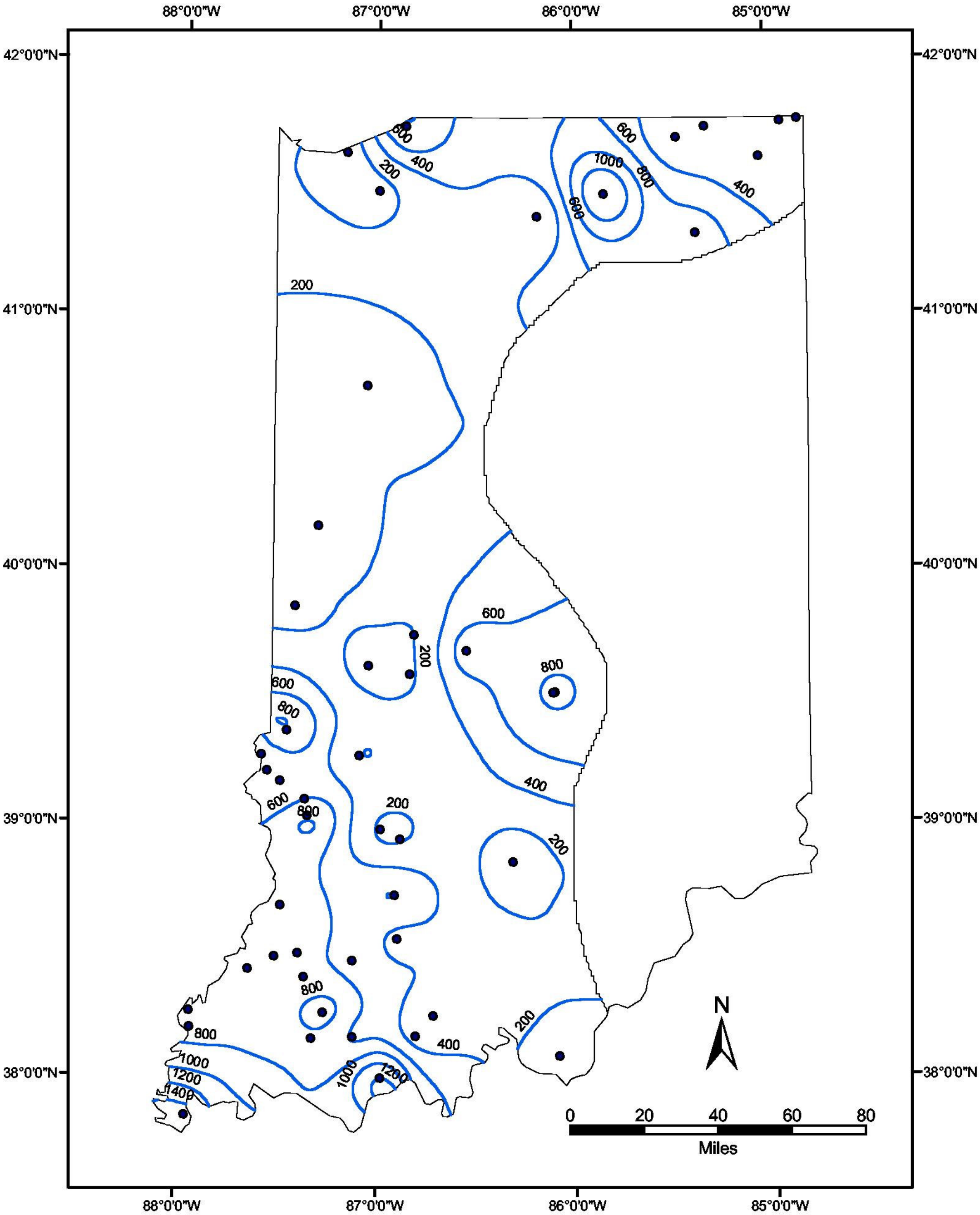

Figure M37. Contour map of thickness of Unit 2 in Indiana.

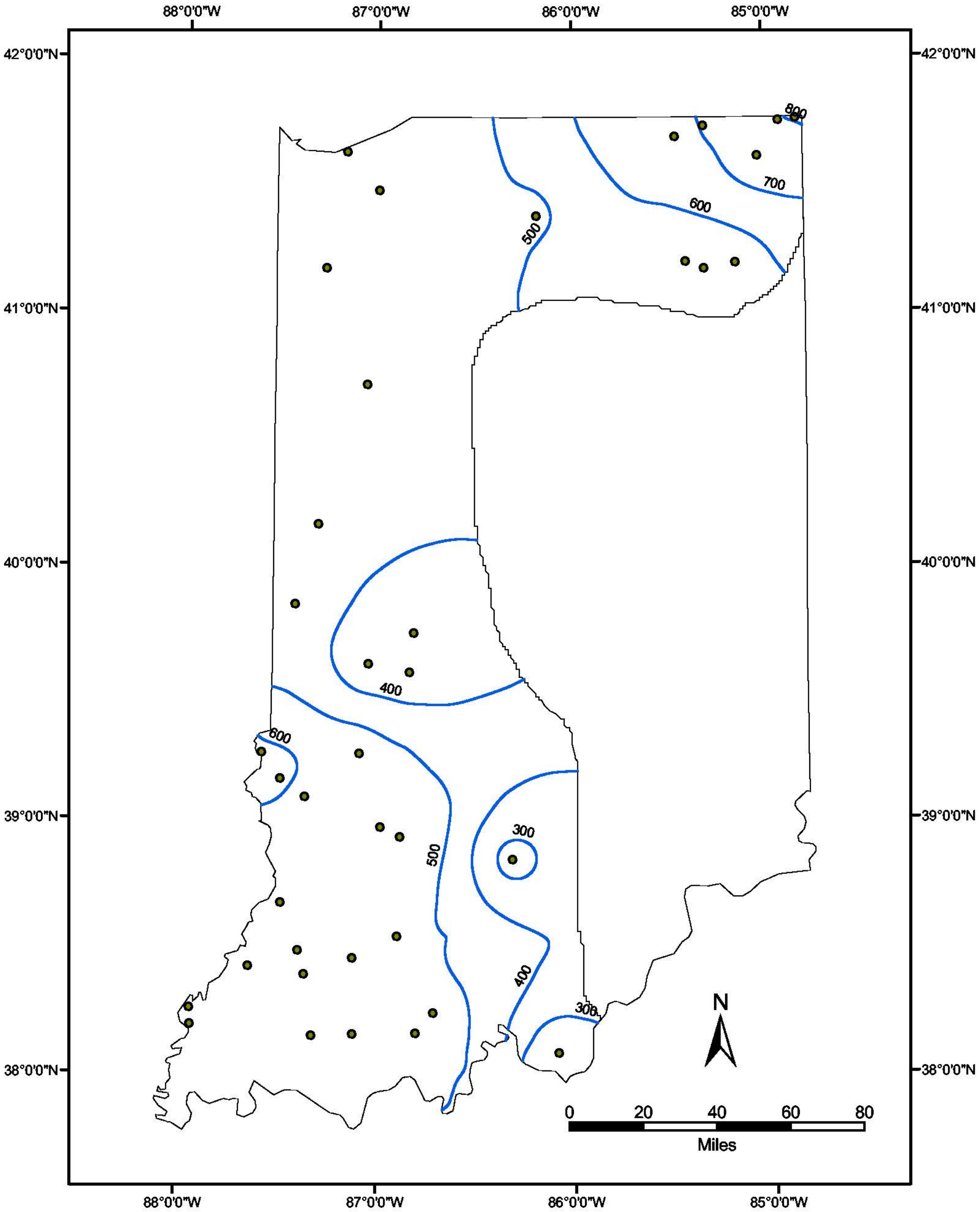

Figure M38. Contour map of thickness of Unit 4 in Indiana.

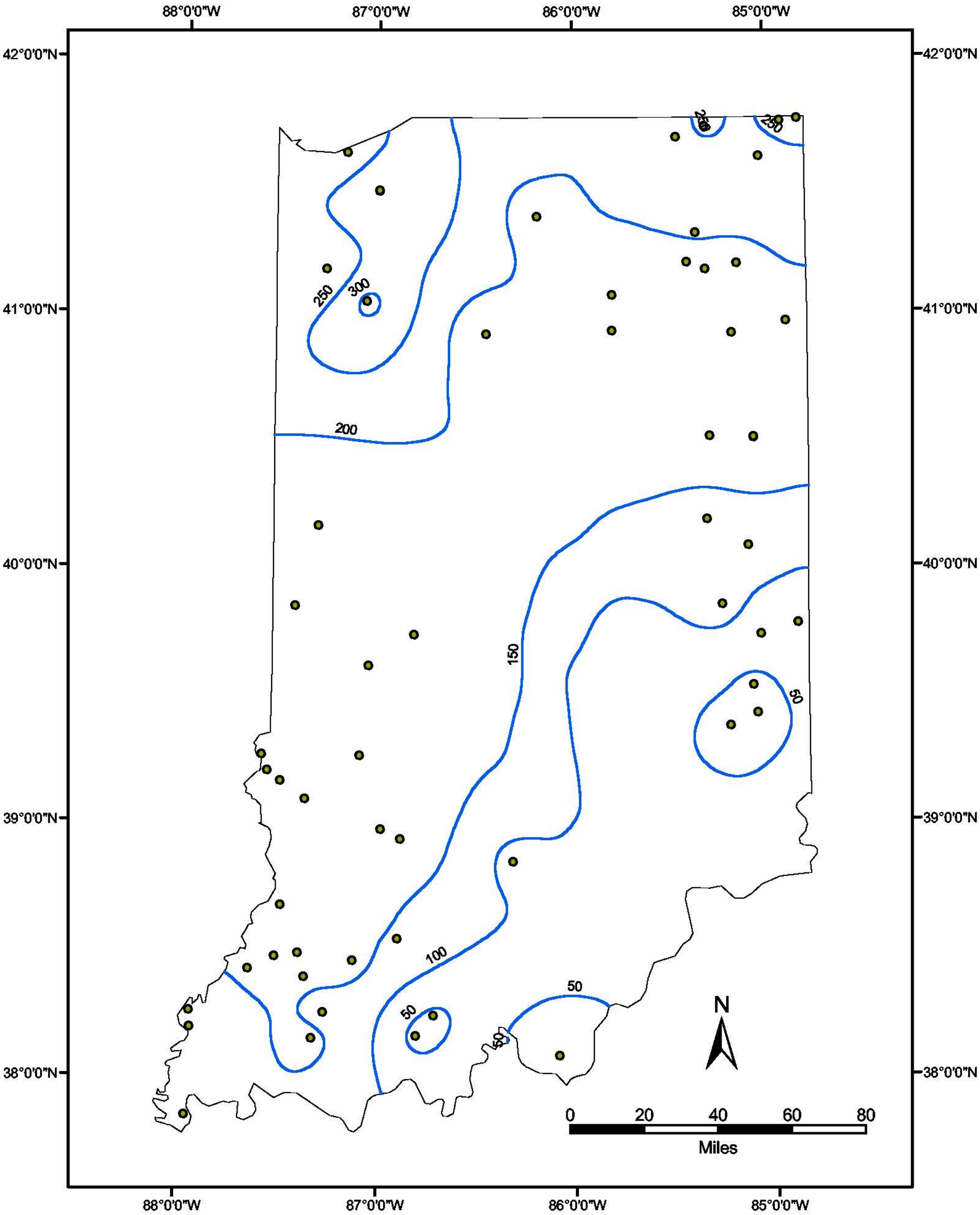

Figure M39. Contour map of thickness of Unit 5 in Indiana.

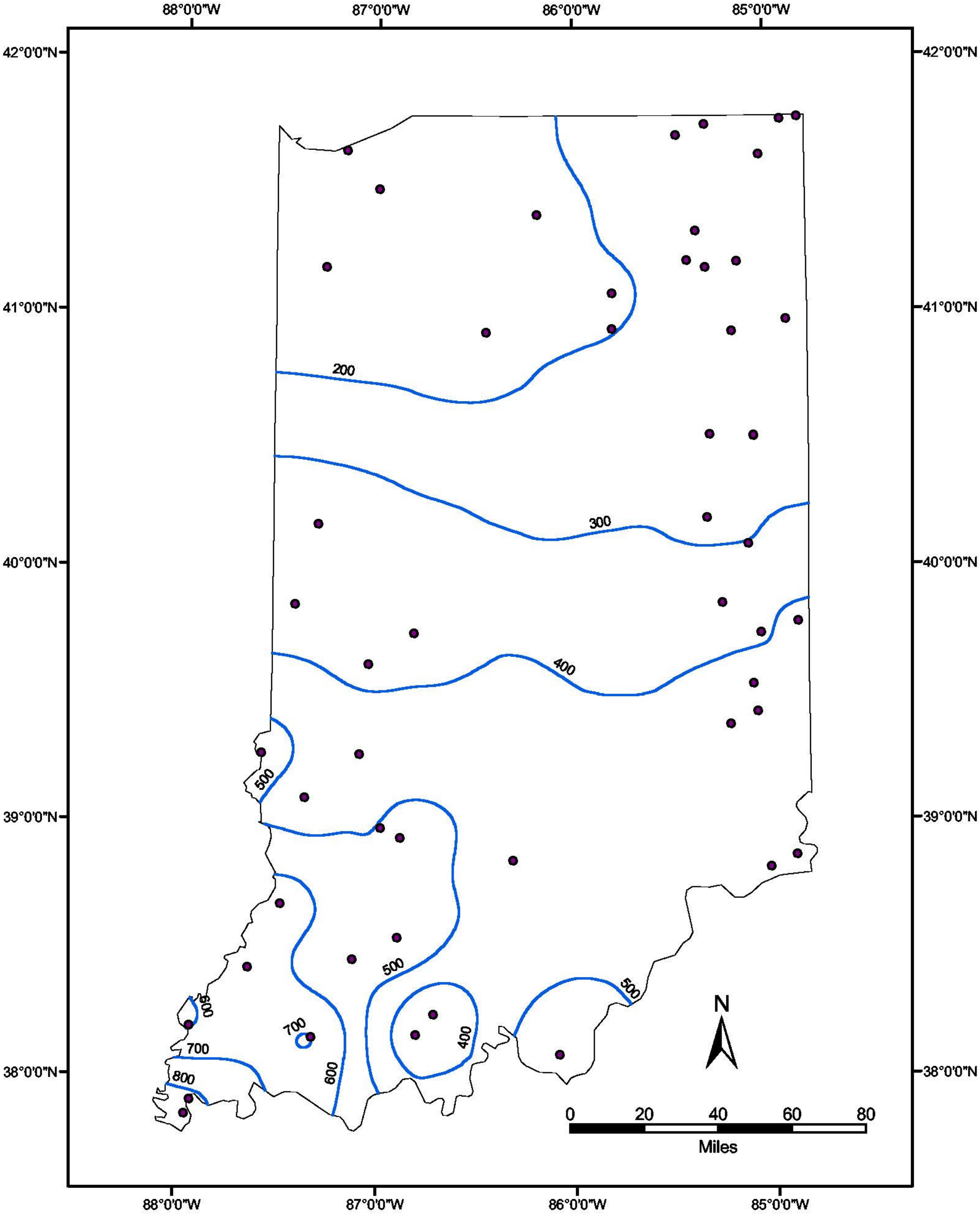

Figure M40. Contour map of thickness of Unit 6 in Indiana.

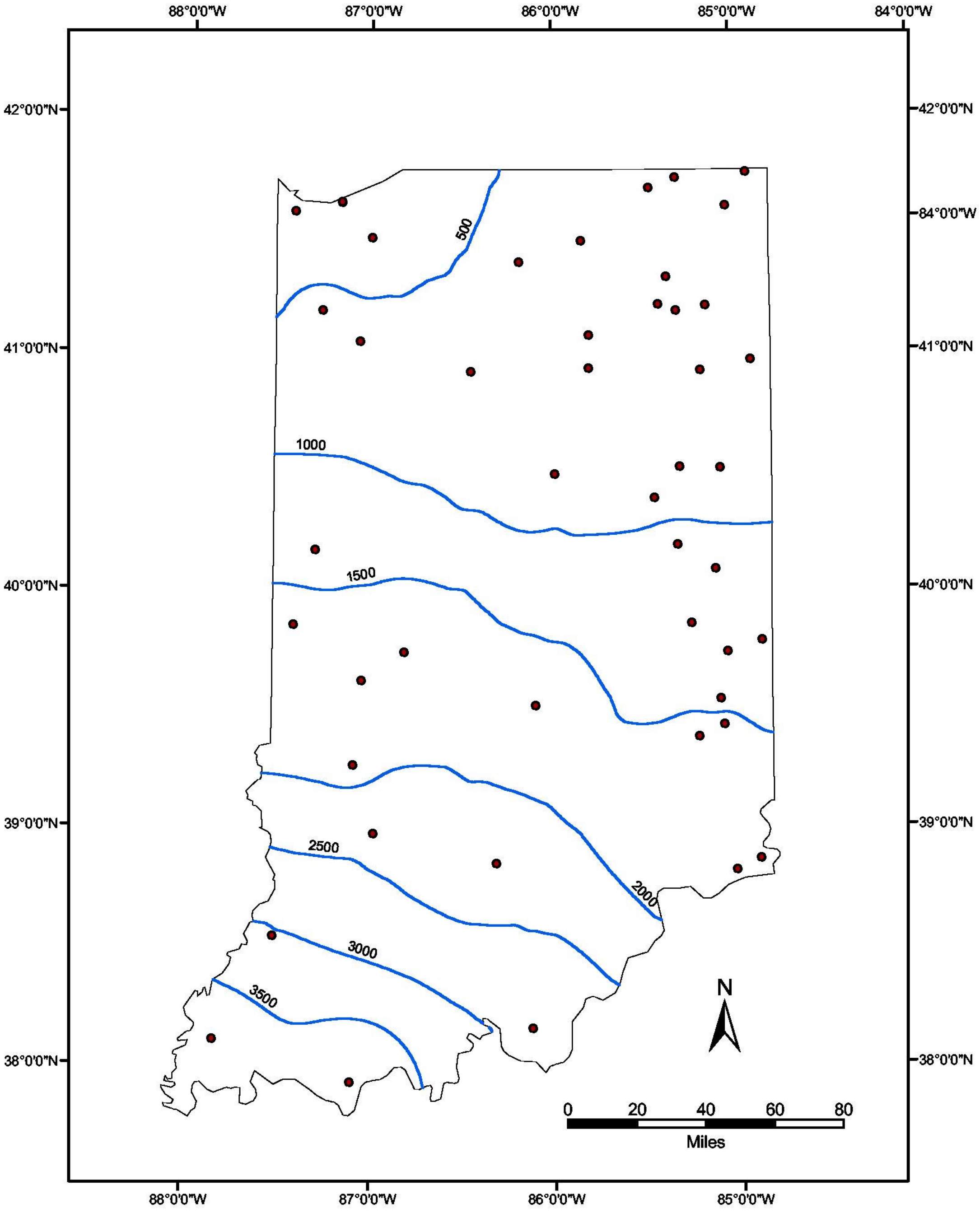

Figure M41. Contour map of thickness of Unit 7 in Indiana.

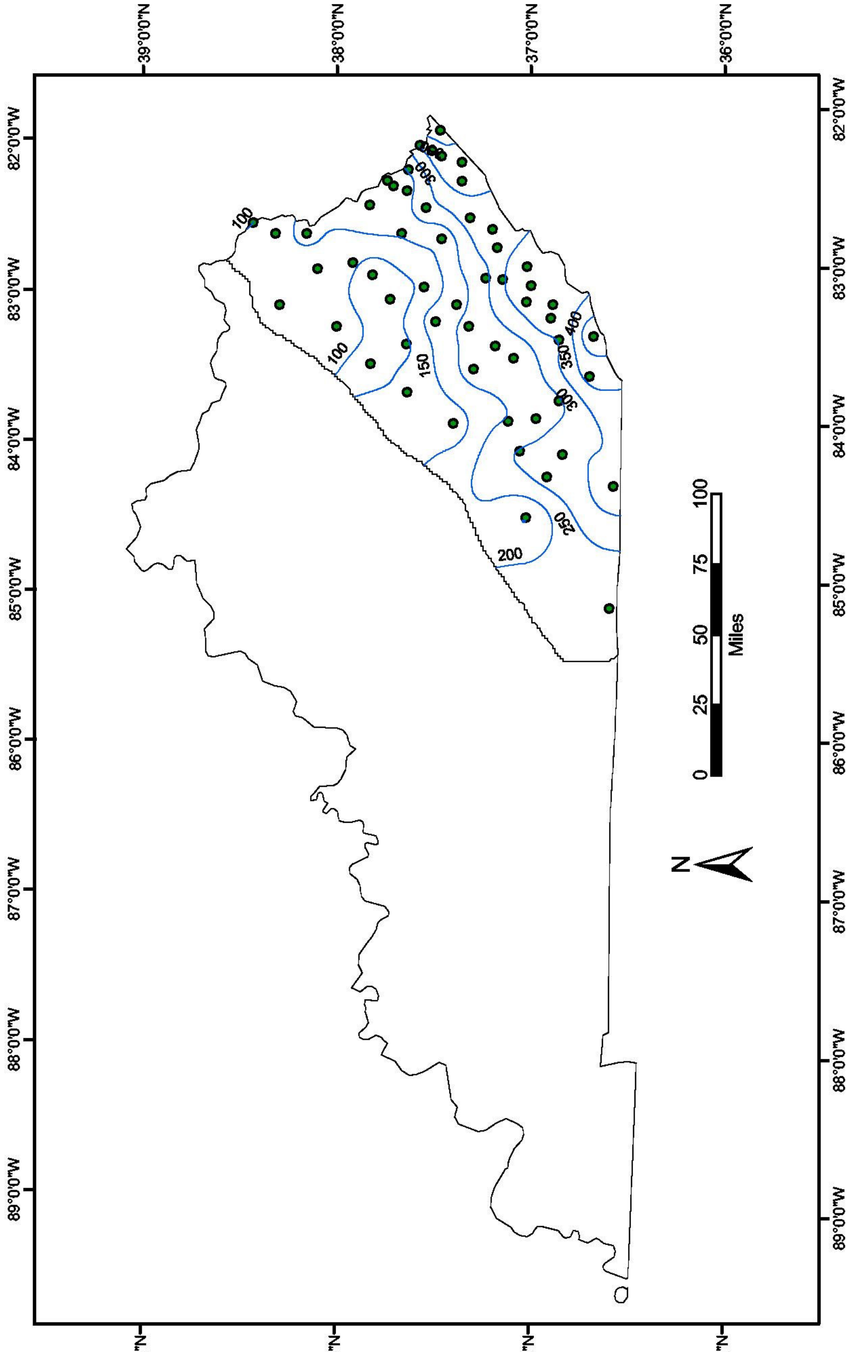

Figure M42. Contour map of thickness of Unit 1 in Kentucky

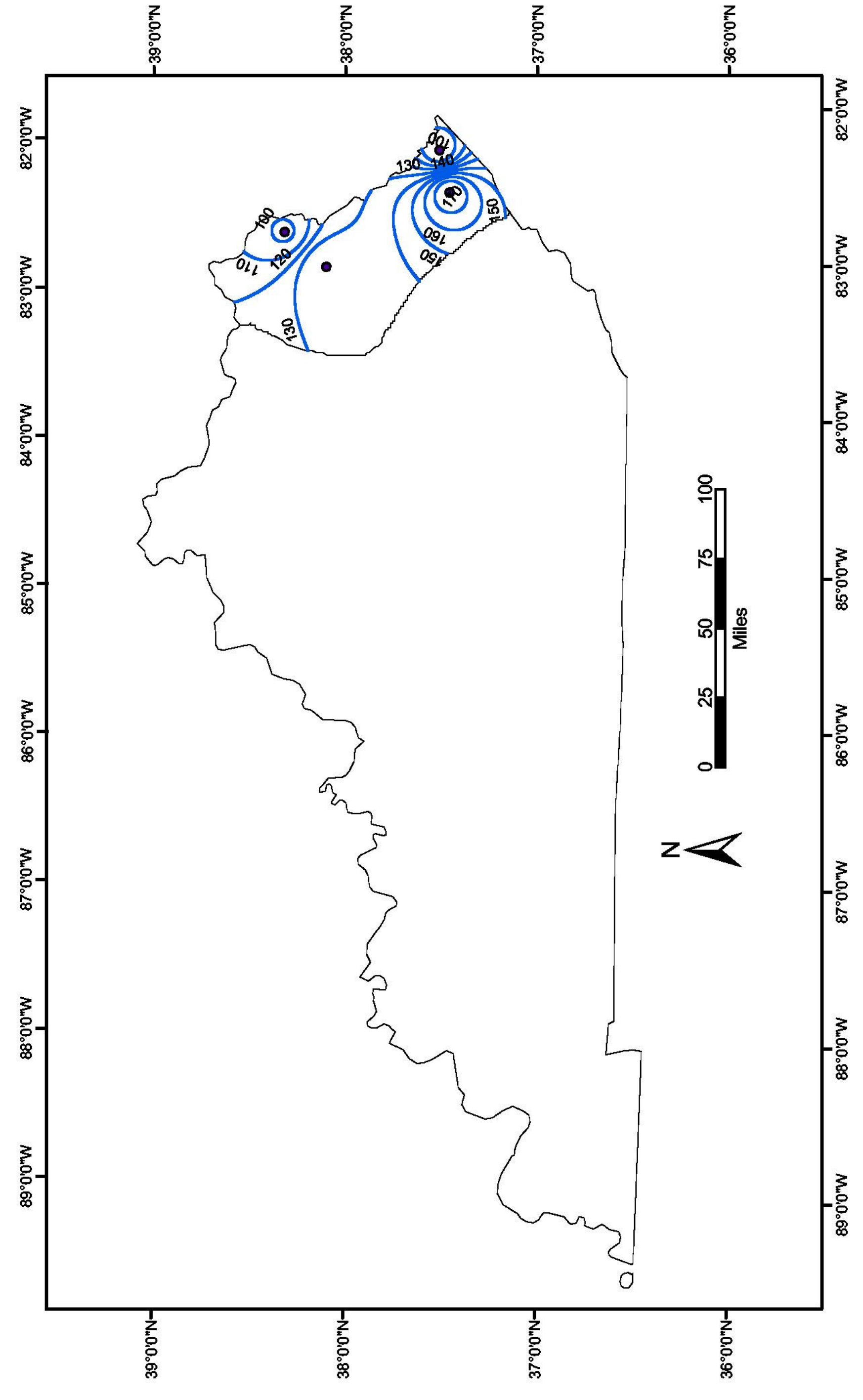

Figure M43. Contour map of thickness of Unit 2/3 in Kentucky

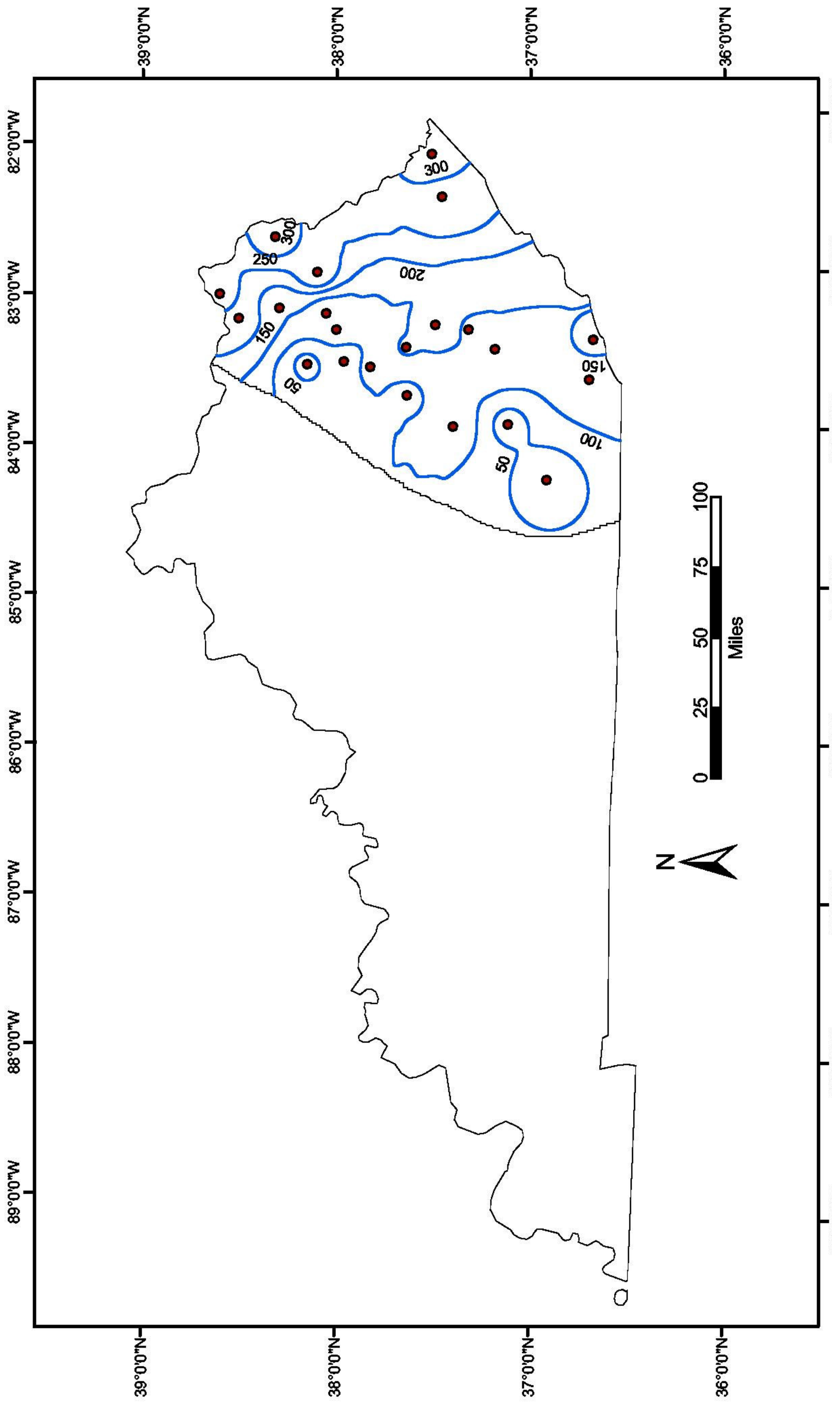

Figure M44. Contour map of thickness of Unit 4 in Kentucky

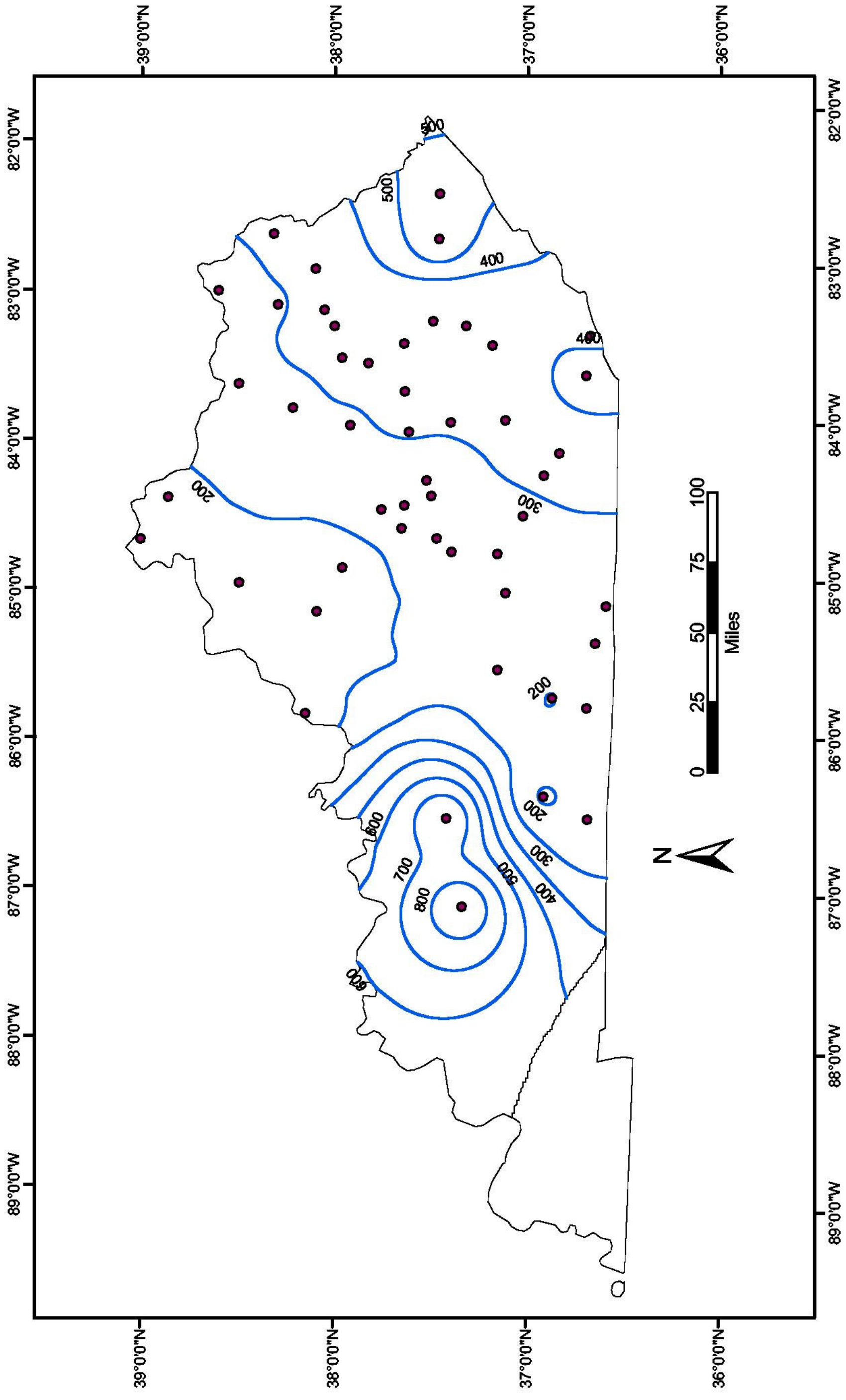

Figure M45. Contour map of thickness of Unit 5 in Kentucky

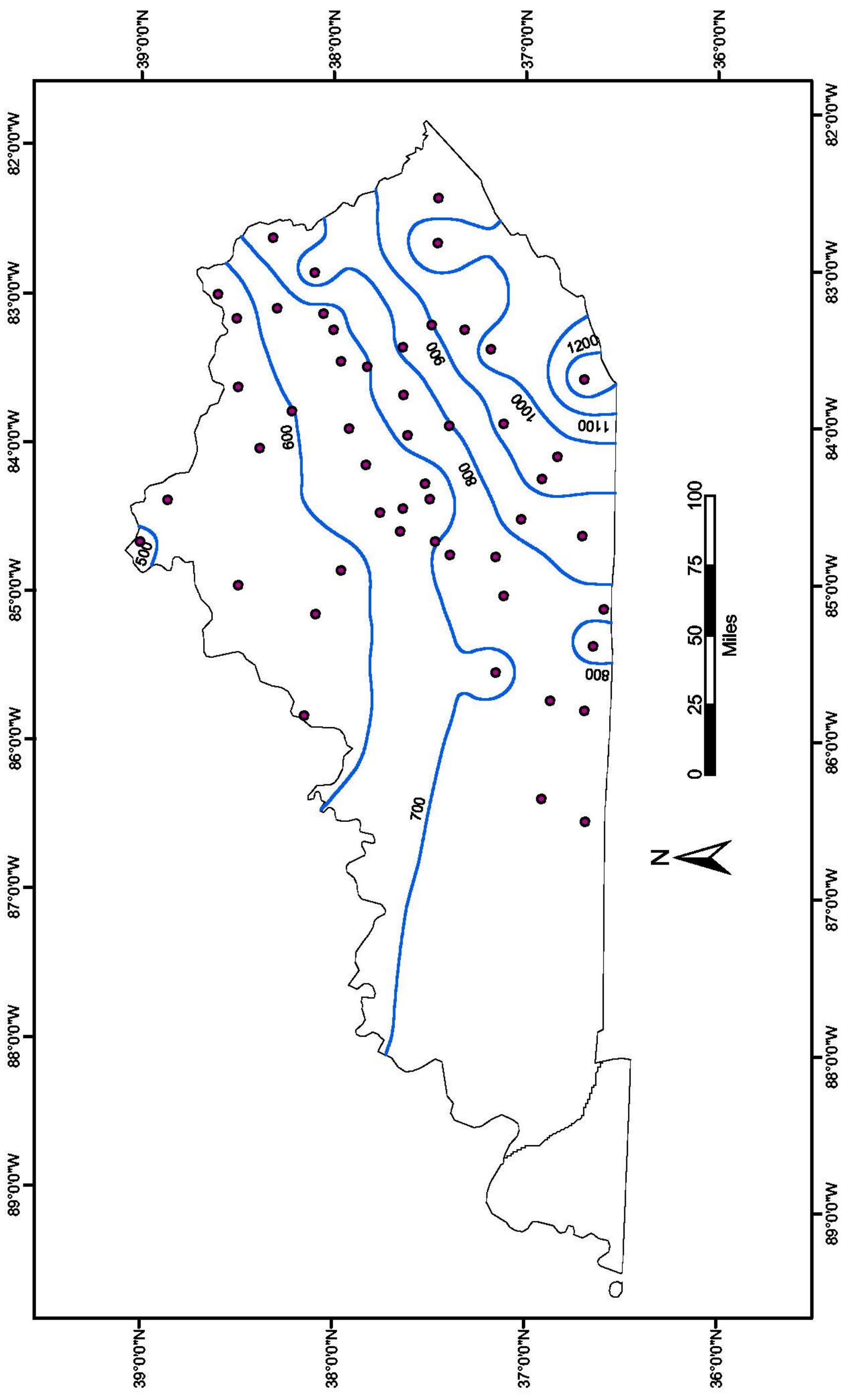

Figure M46. Contour map of thickness of Unit 6 in Kentucky

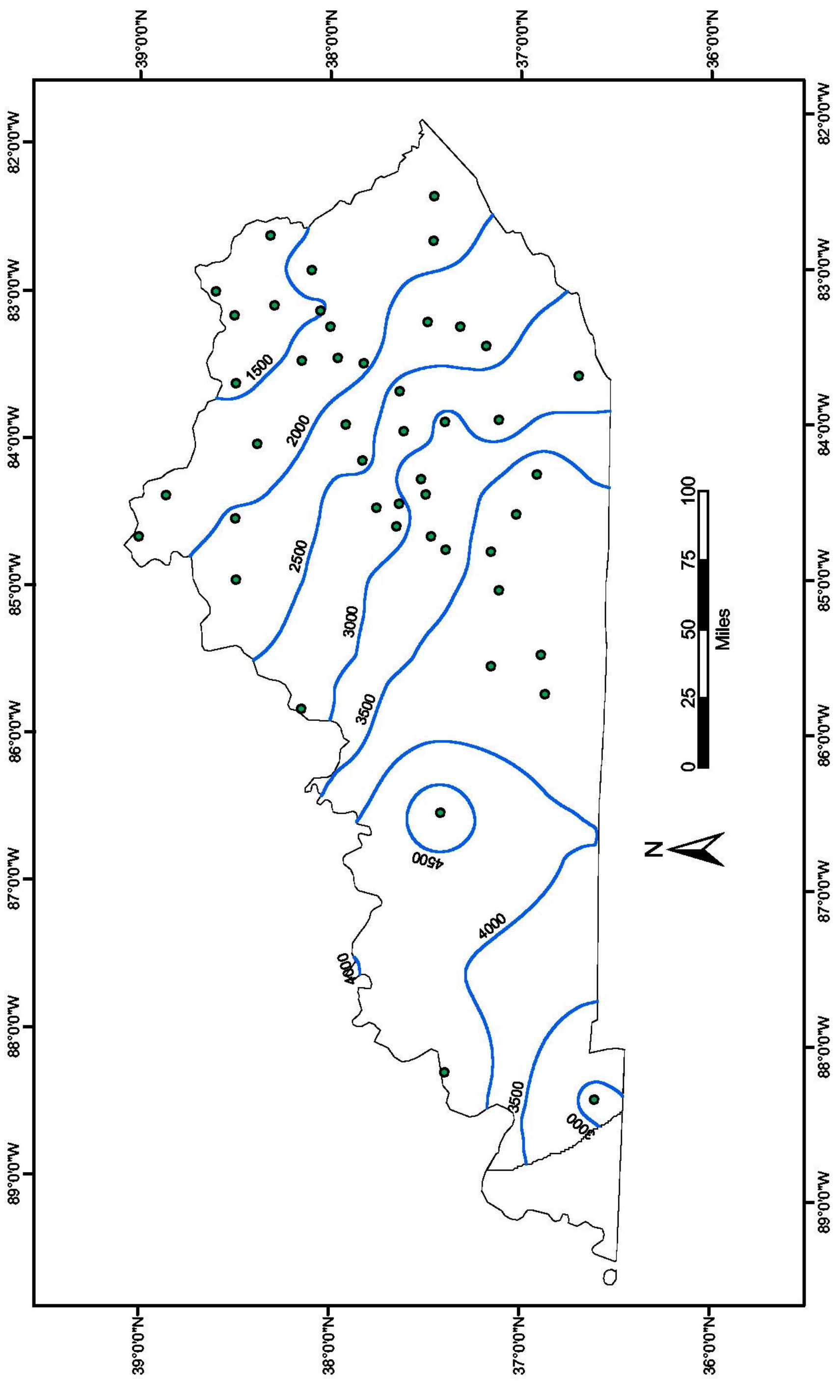

Figure M47. Contour map of thickness of Unit 7 in Kentucky

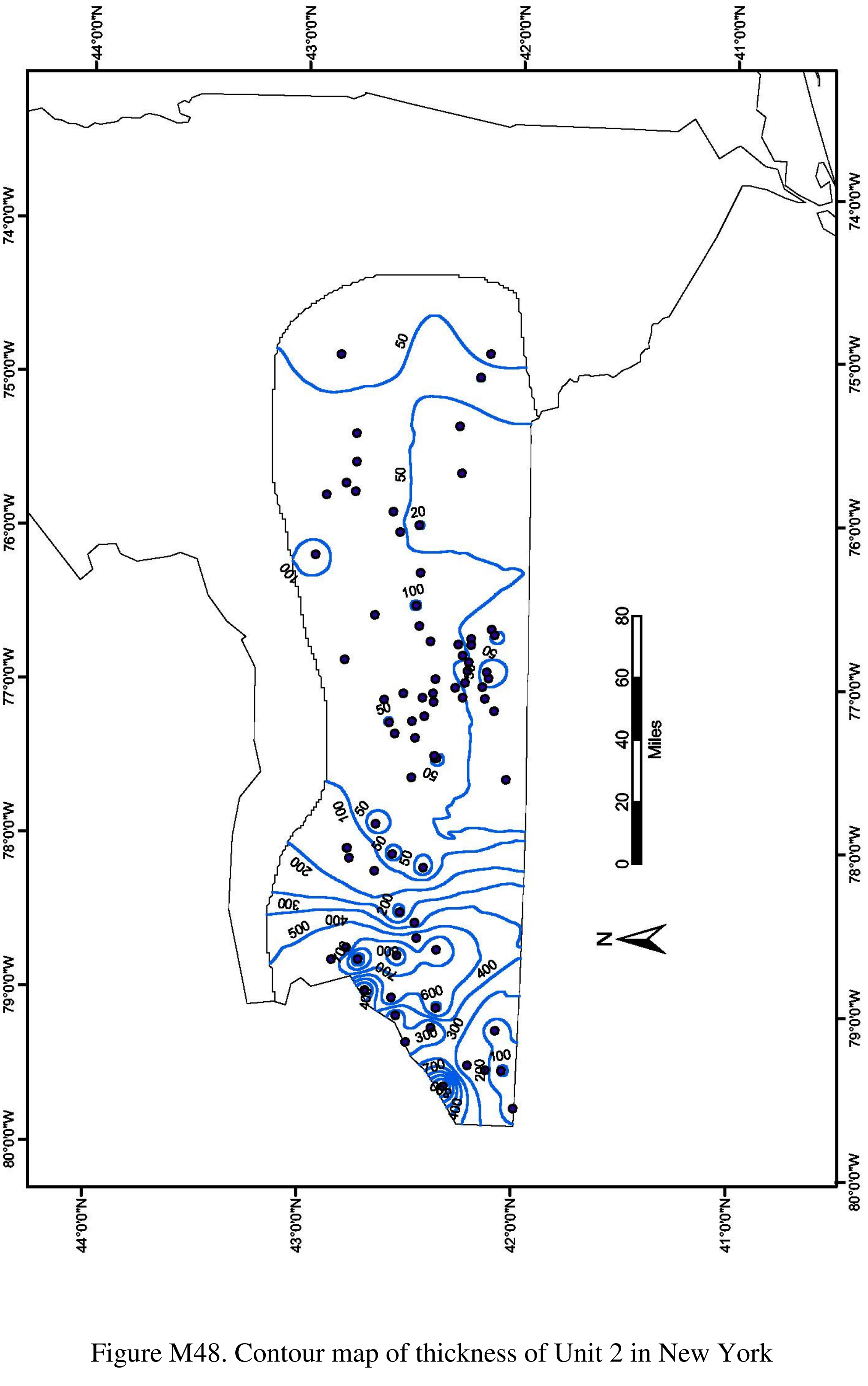

Figure M48. Contour map of thickness of Unit 2 in New York

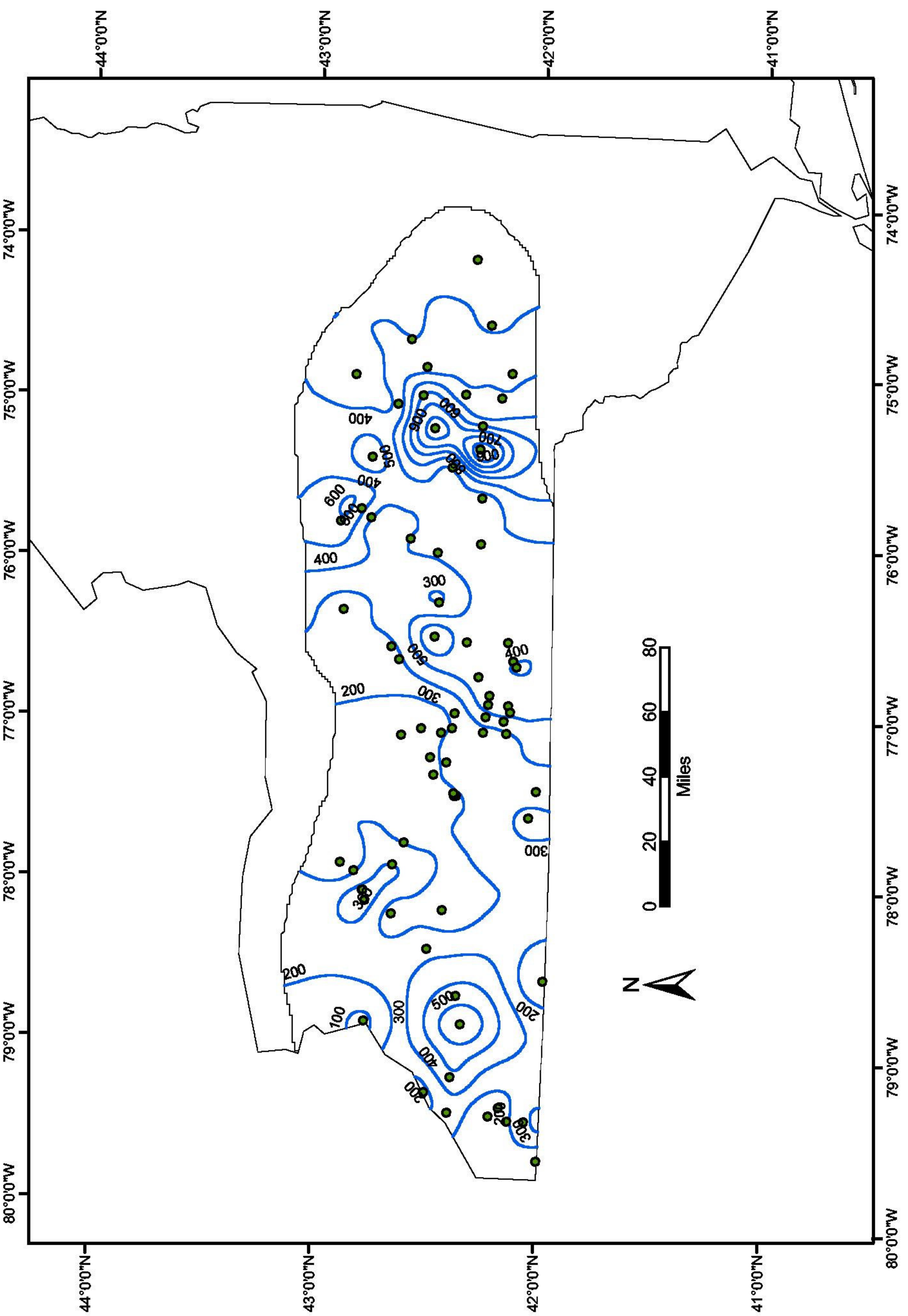

Figure M49. Contour map of thickness of Unit 3 in New York

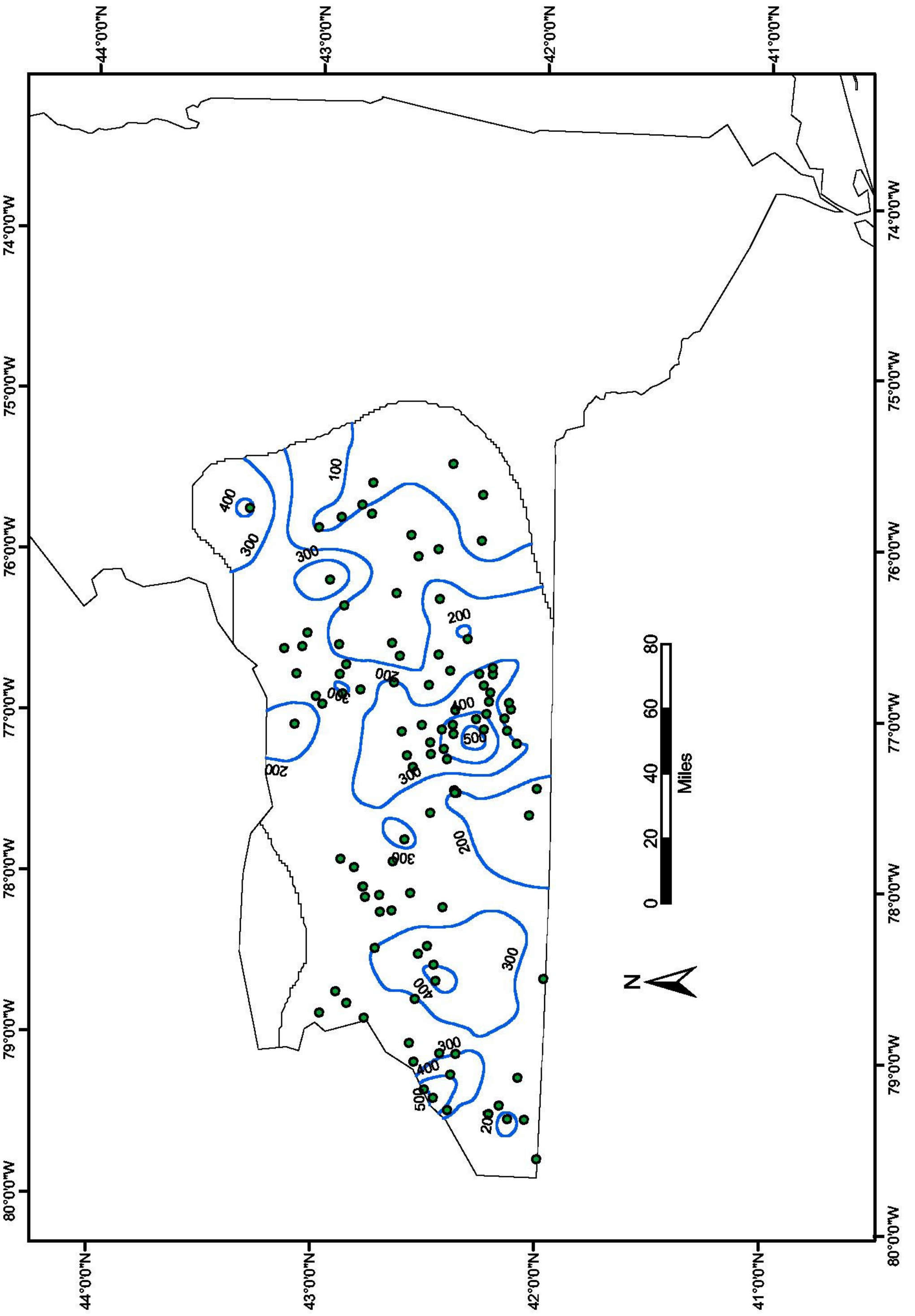

Figure M50. Contour map of thickness of Unit 4 in New York

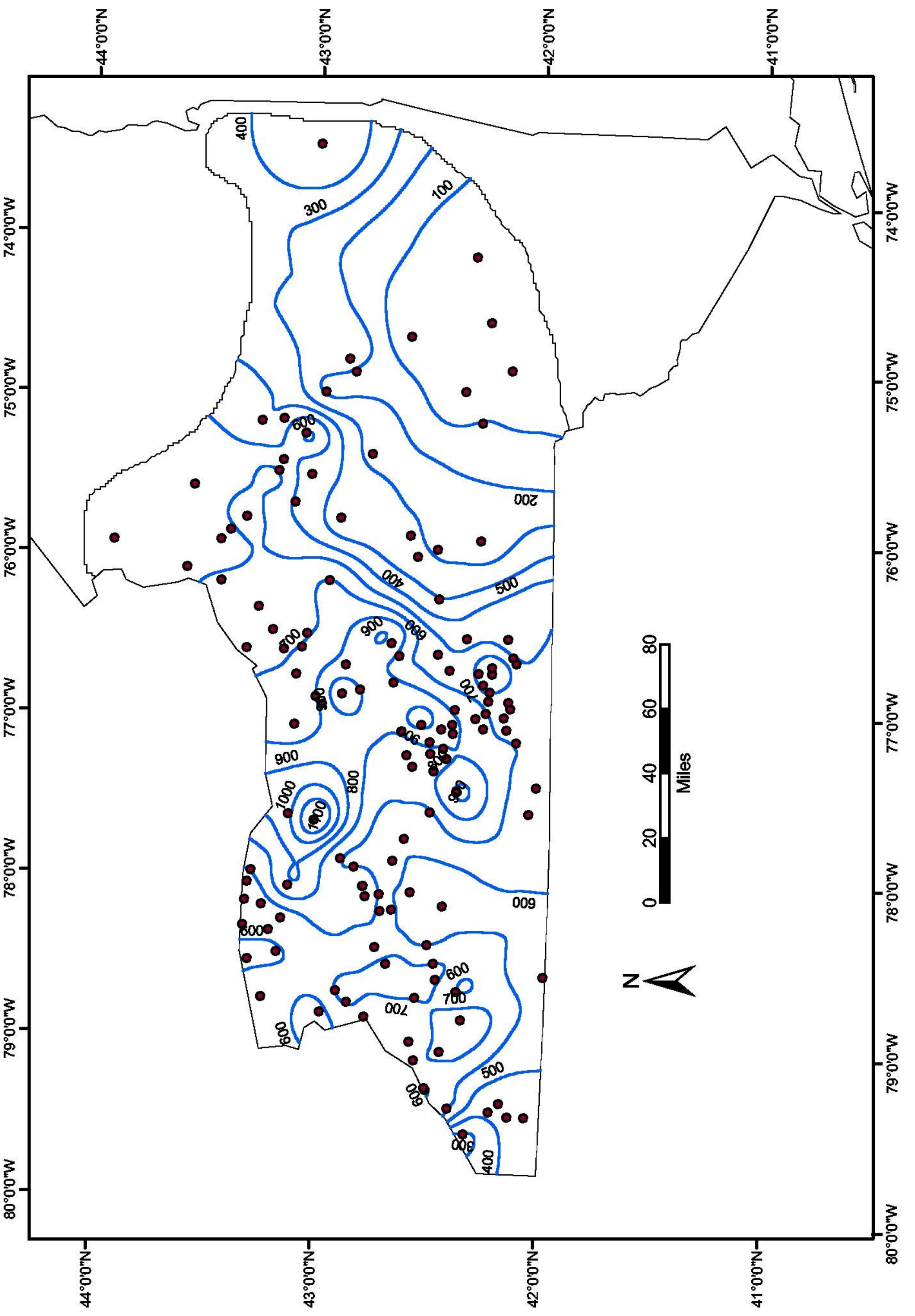

Figure M51. Contour map of thickness of Unit 5 in New York

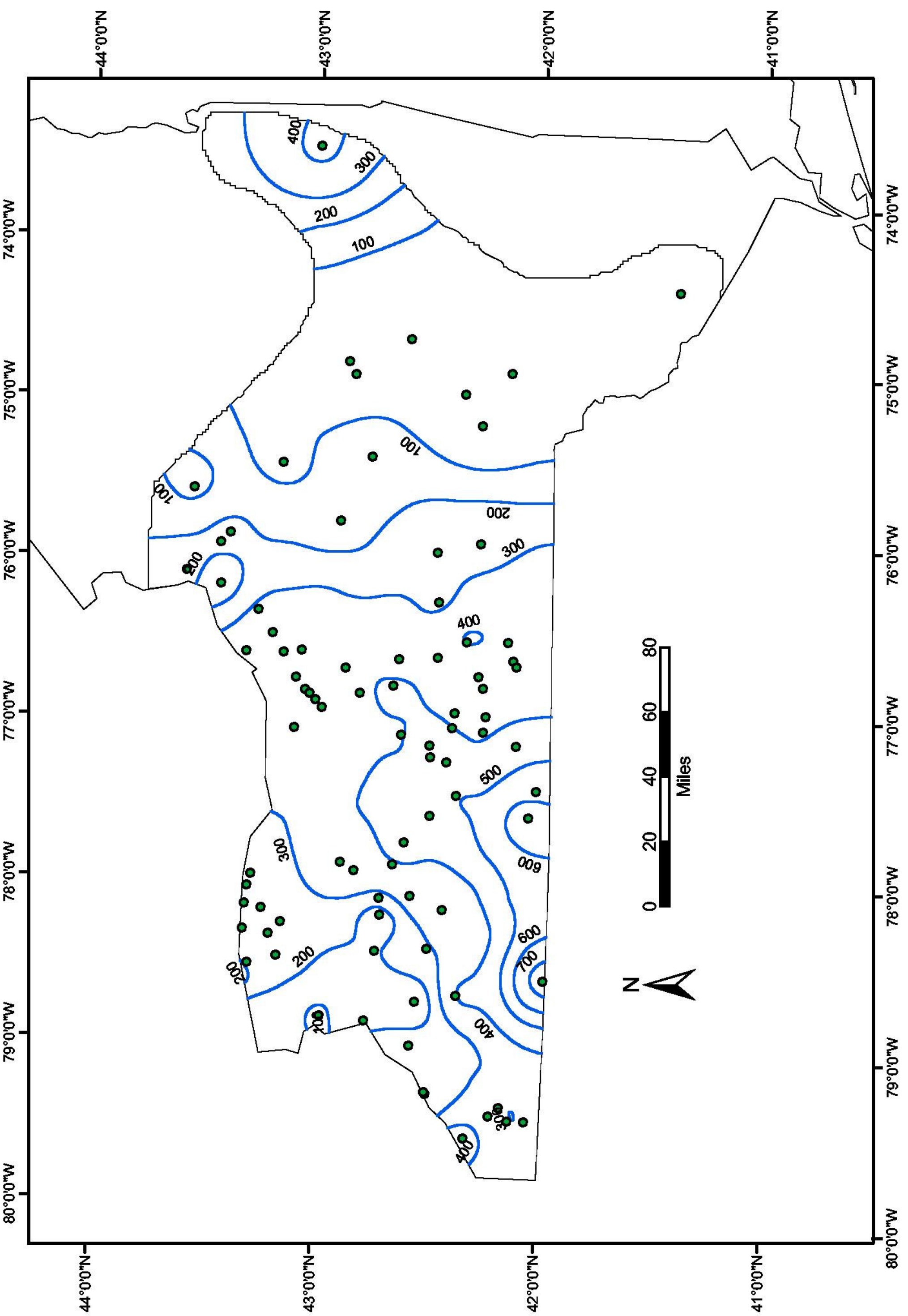

Figure M52. Contour map of thickness of Unit 6 in New York

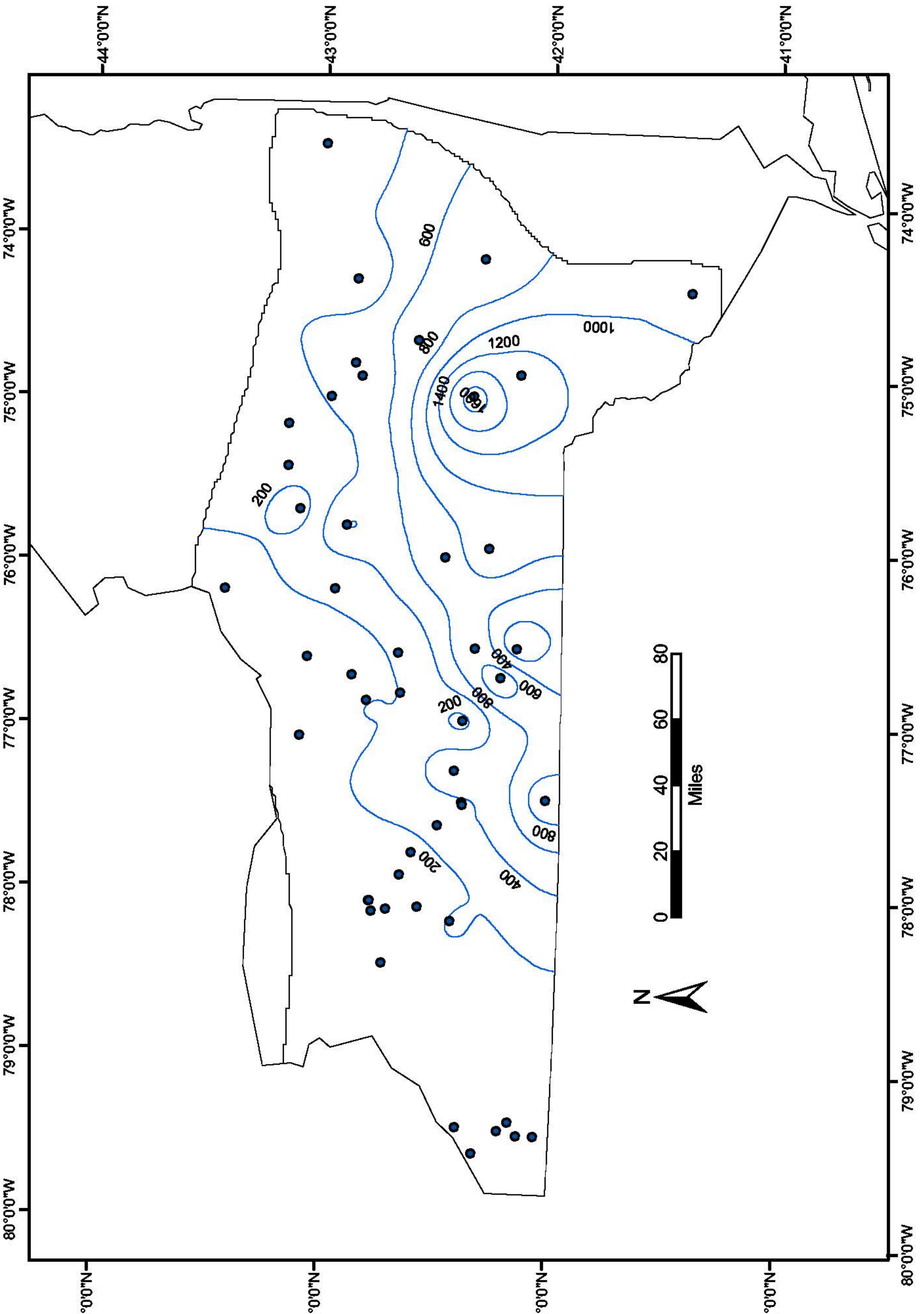

Figure M53. Contour map of thickness of Unit 7 in New York

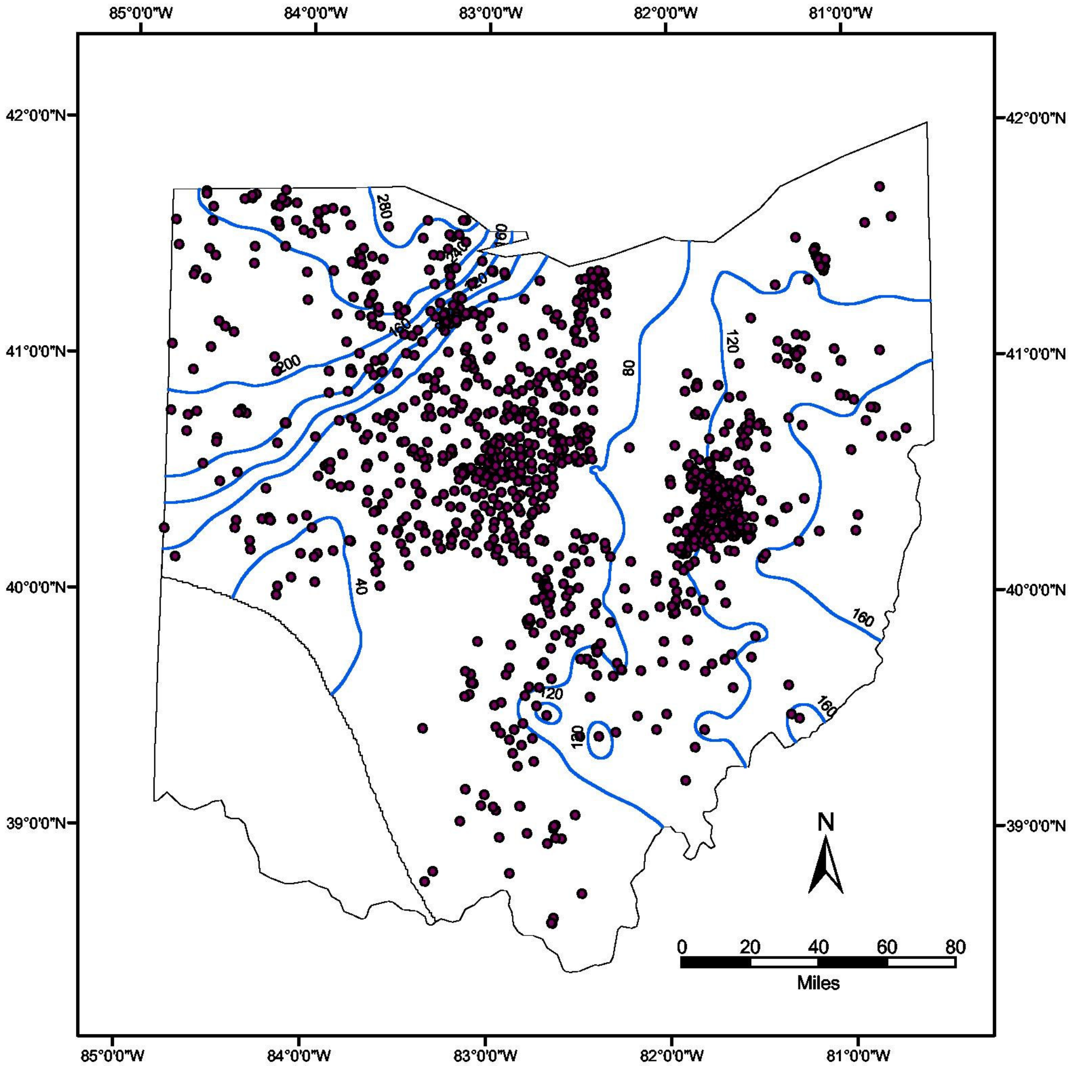

Figure M54. Contour map of thickness of Unit 5 in Ohio

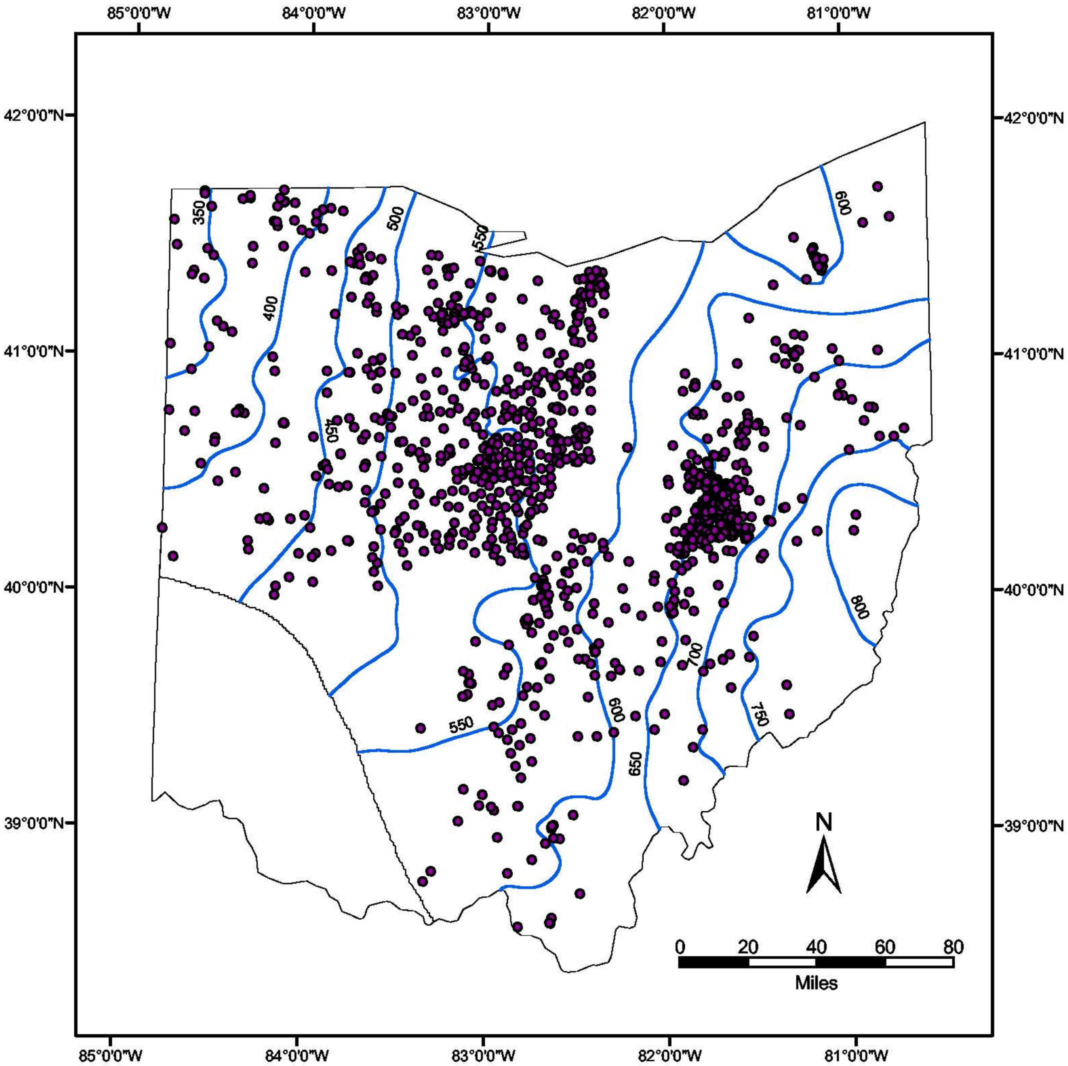

Figure M55. Contour map of thickness of Unit 6 in Ohio

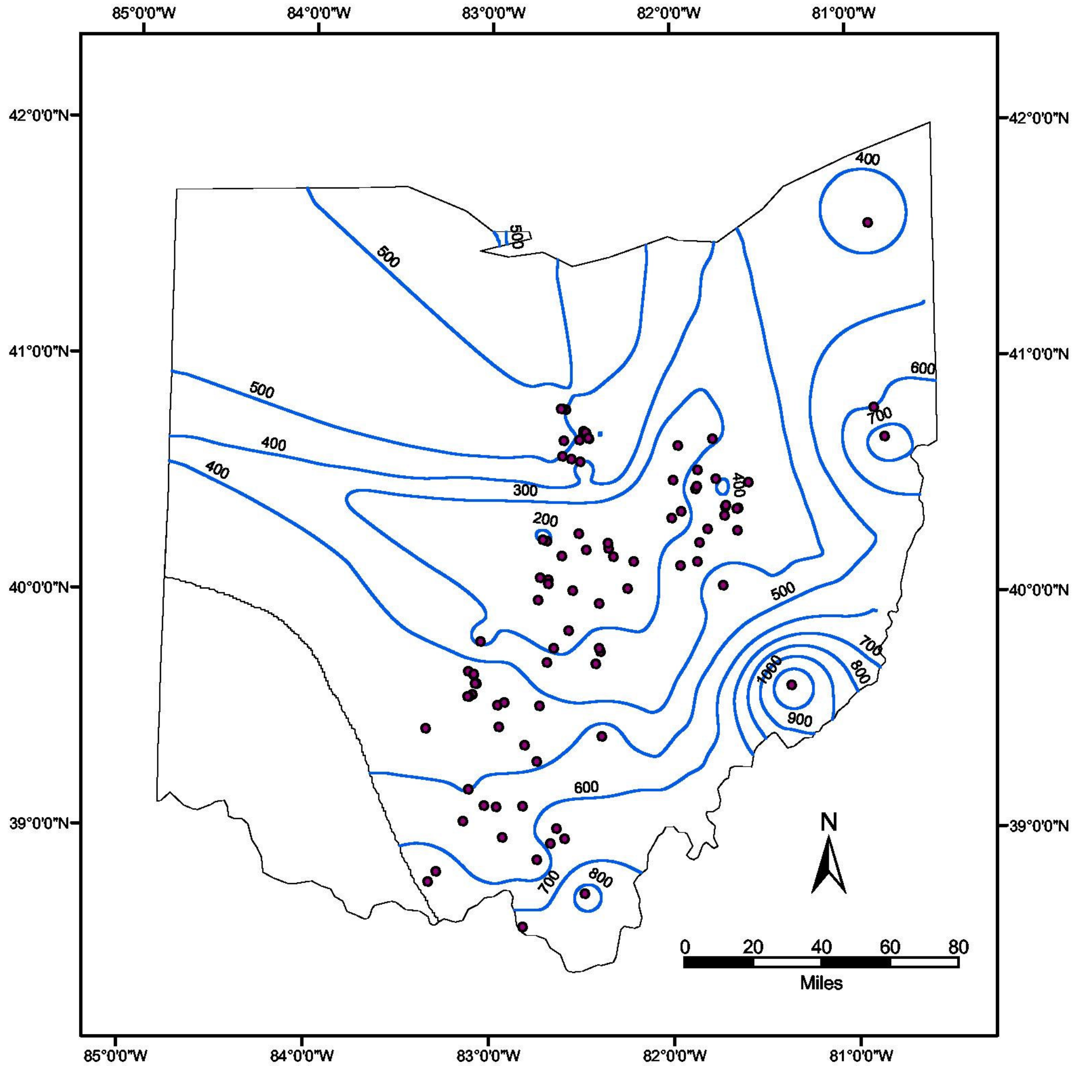

Figure M56. Contour map of thickness of Unit 7 in Ohio

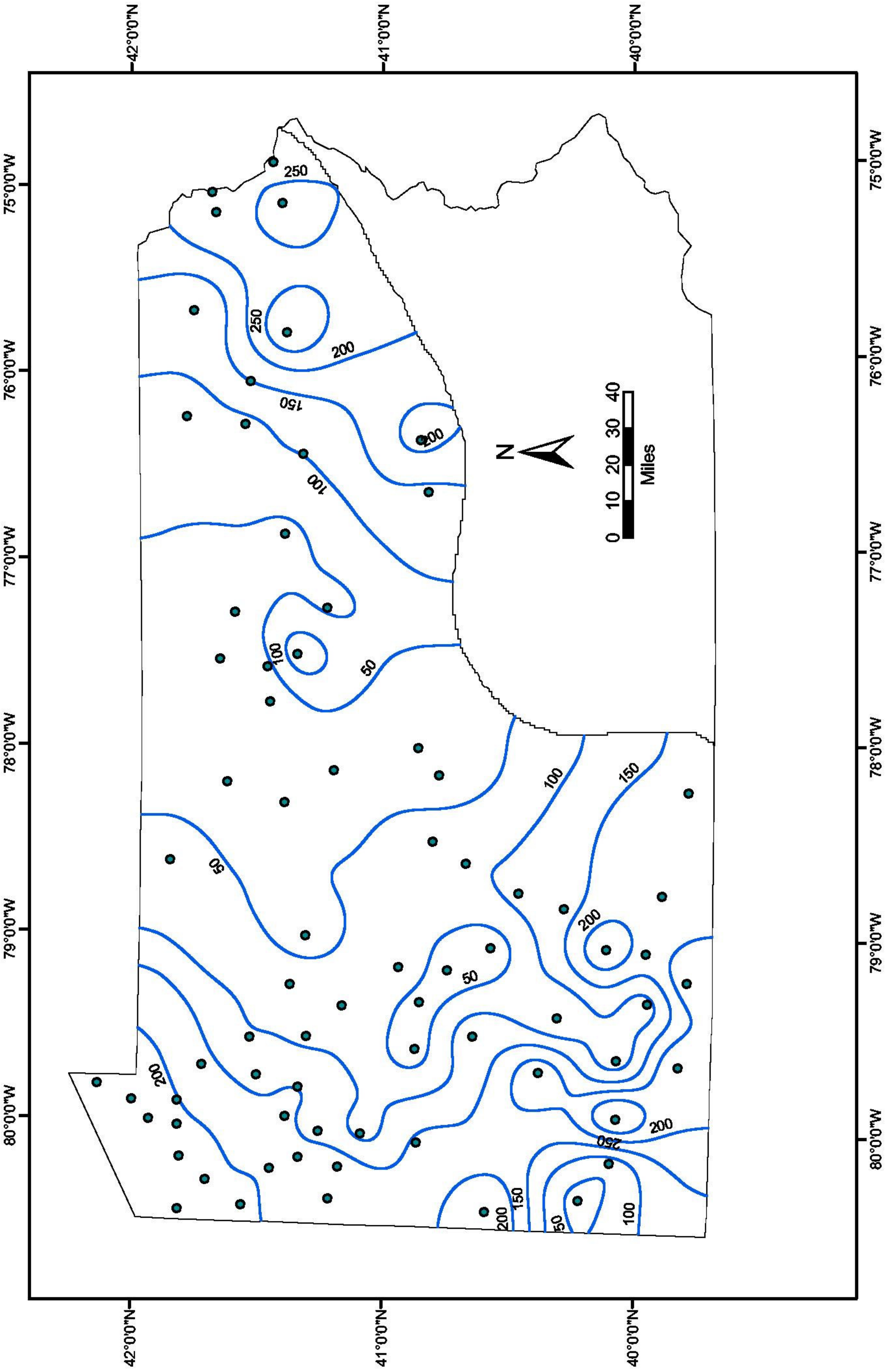

Figure M57. Contour map of thickness of Unit 2 in Pennsylvania

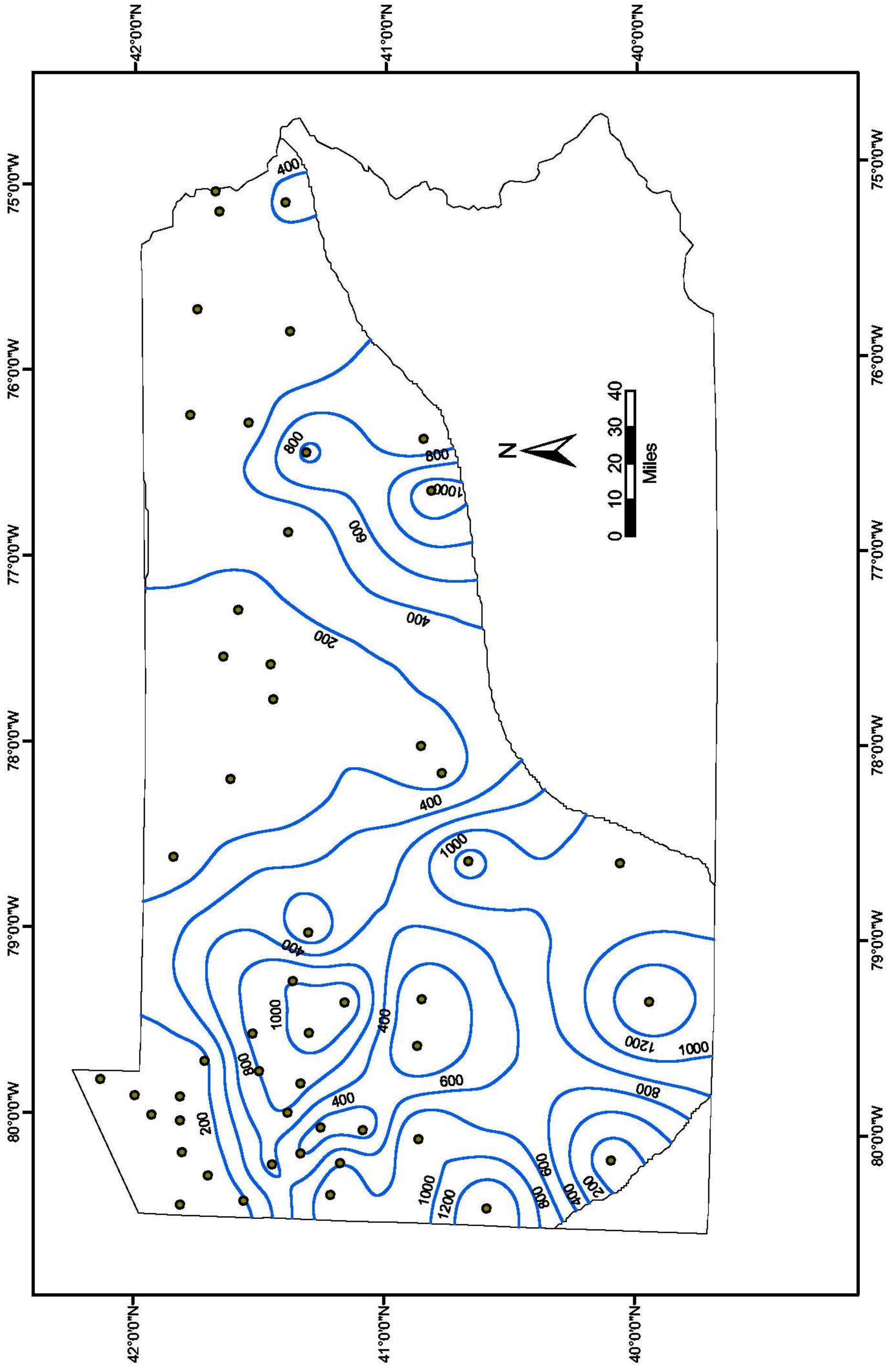

Figure M58. Contour map of thickness of Unit 3 in Pennsylvania

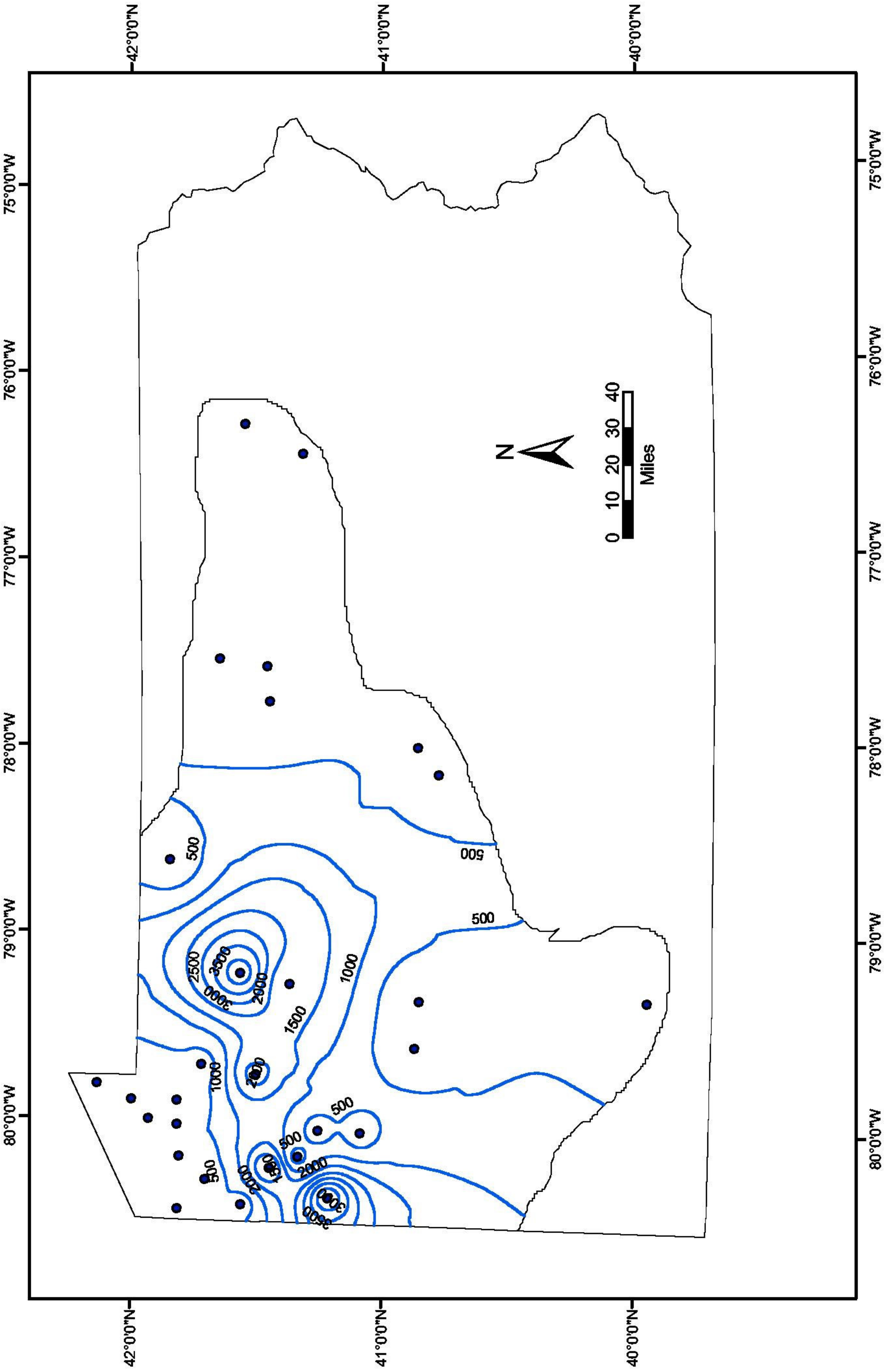

Figure M59. Contour map of thickness of Unit 4 in Pennsylvania

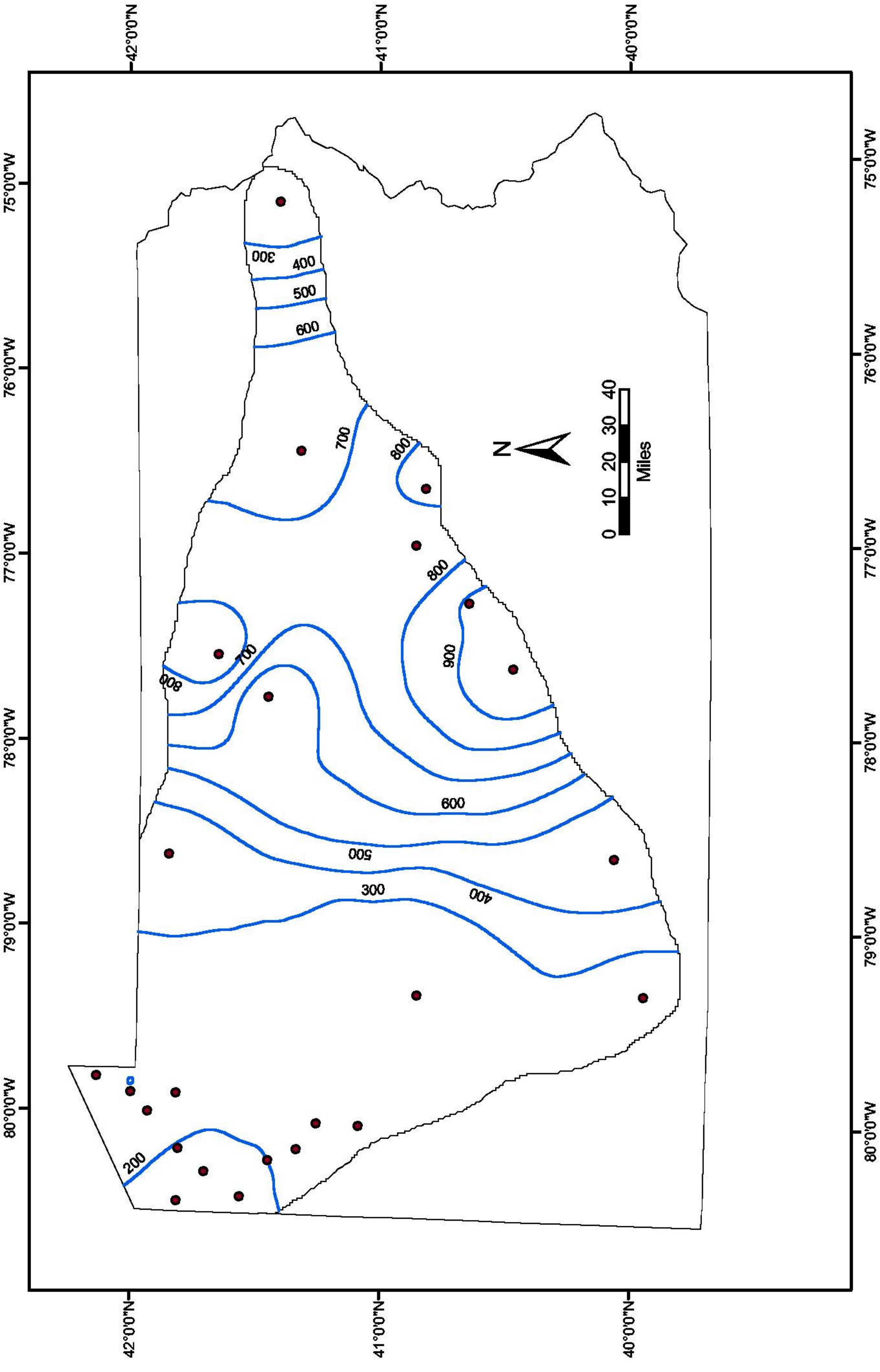

Figure M60. Contour map of thickness of Unit 5 in Pennsylvania

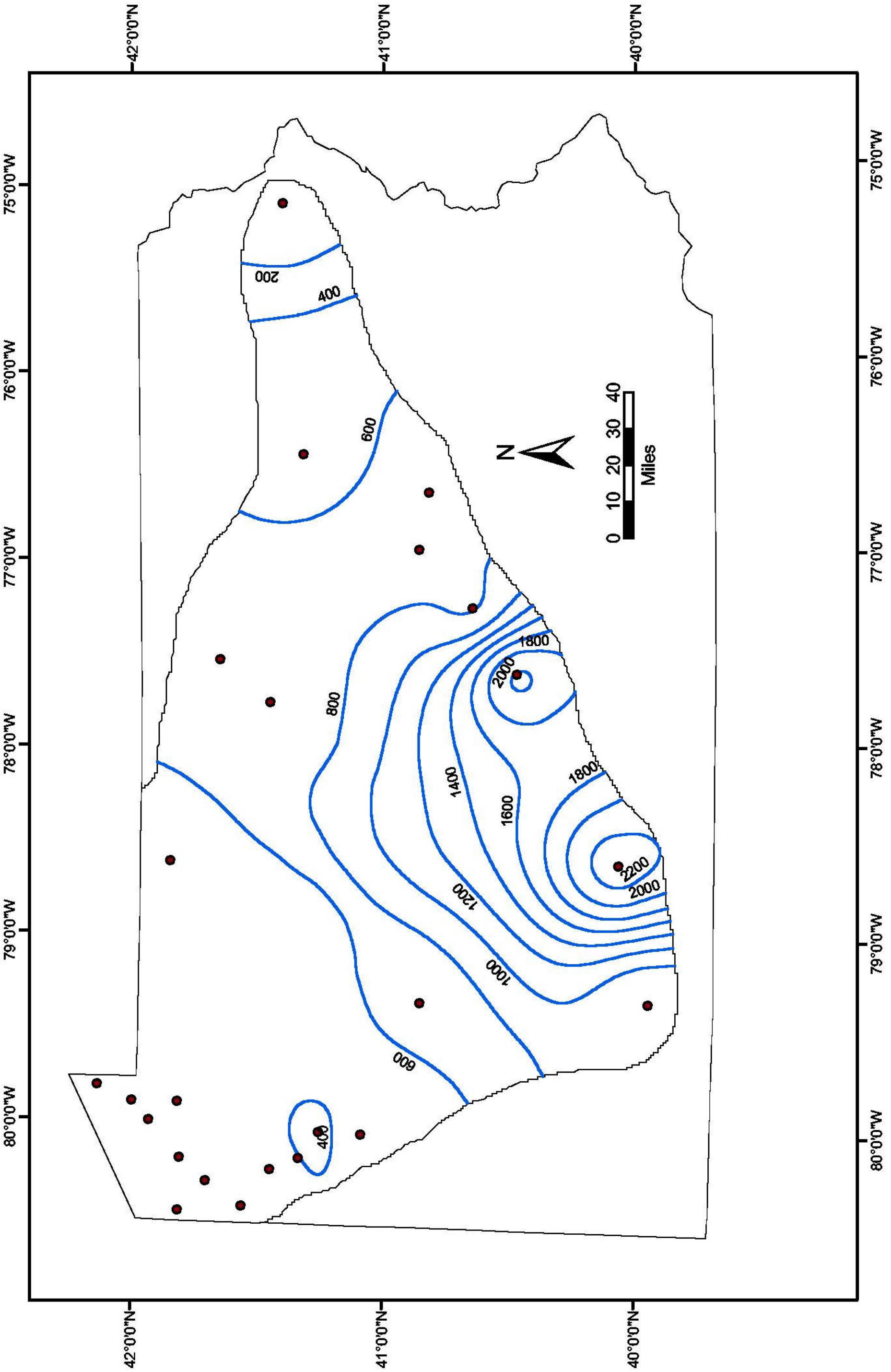

Figure M61. Contour map of thickness of Unit 6 in Pennsylvania

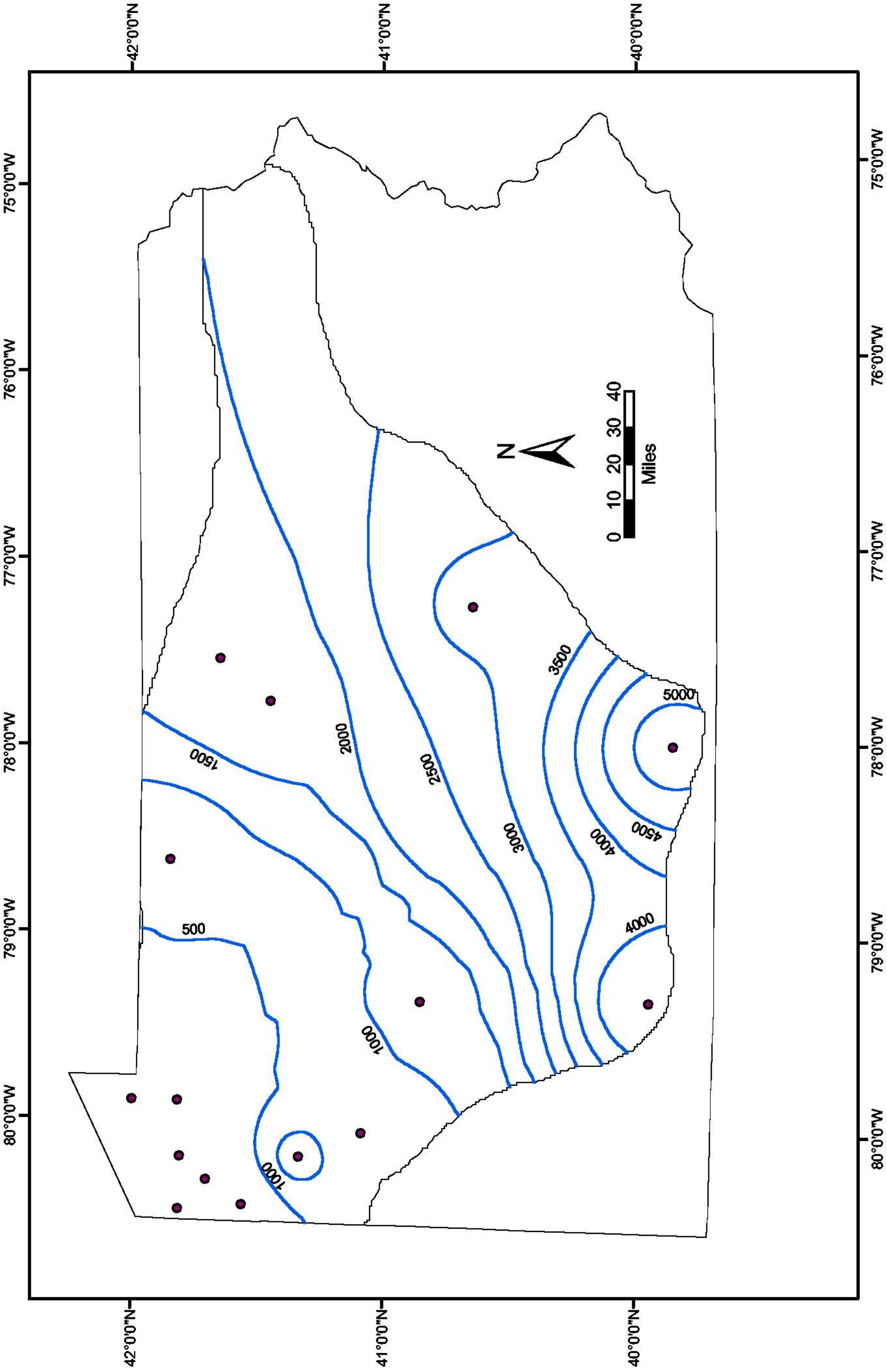

Figure M62. Contour map of thickness of Unit 7 in Pennsylvania

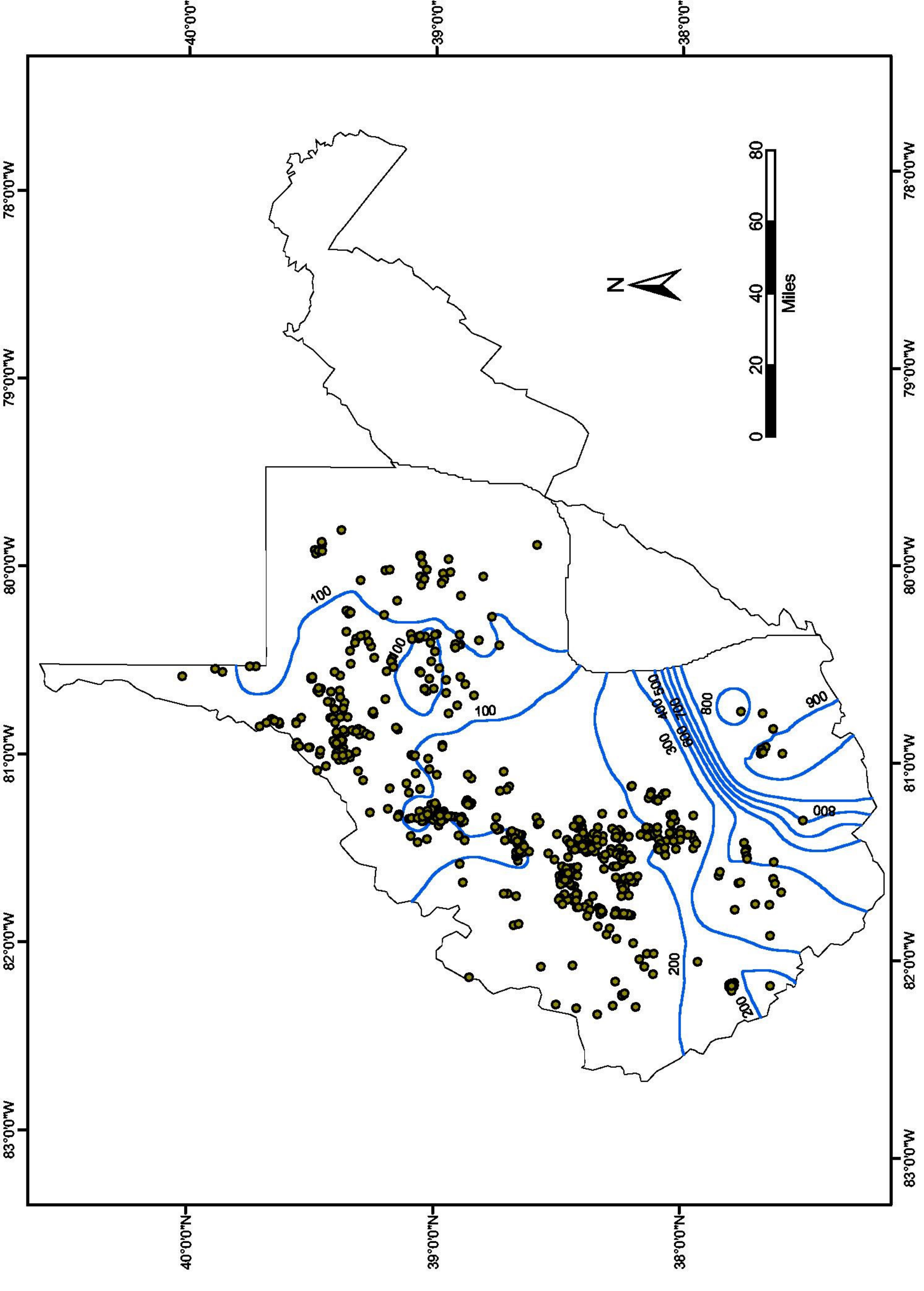

Figure M63. Contour map of thickness of Unit 1 in West Virginia

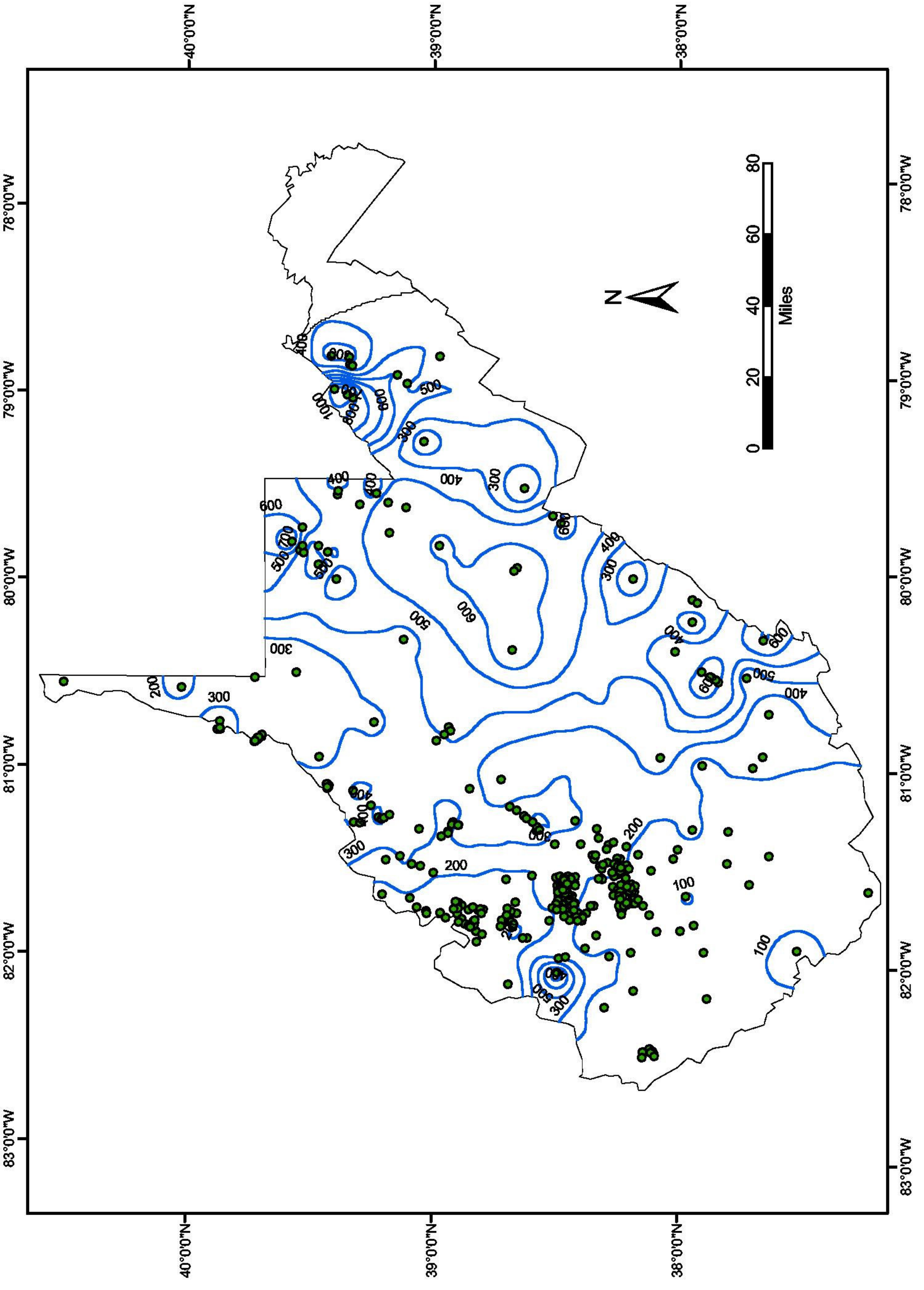

Figure M64. Contour map of thickness of Subunit 3a in West Virginia

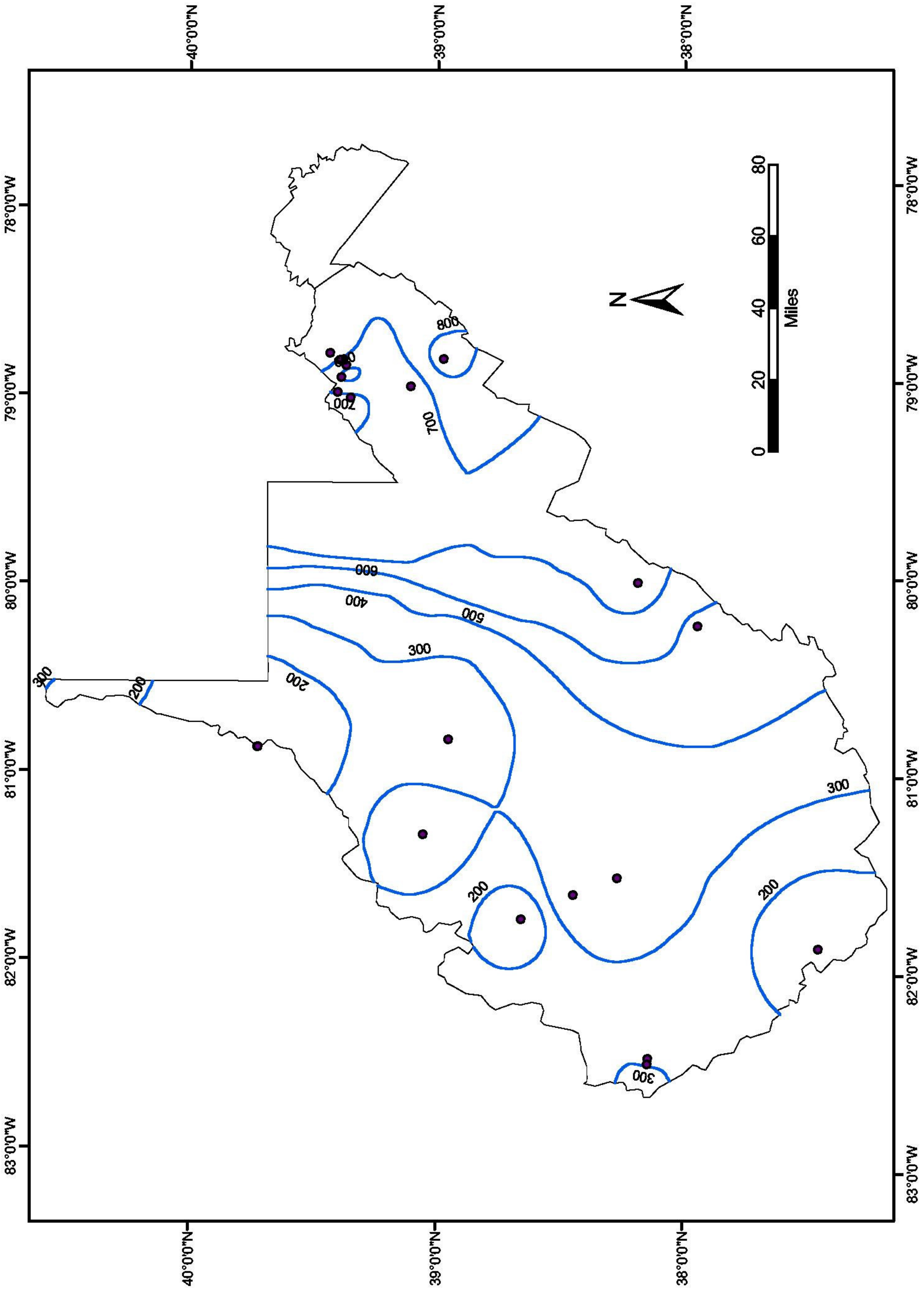

Figure M65. Contour map of thickness of Subunit 3b in West Virginia

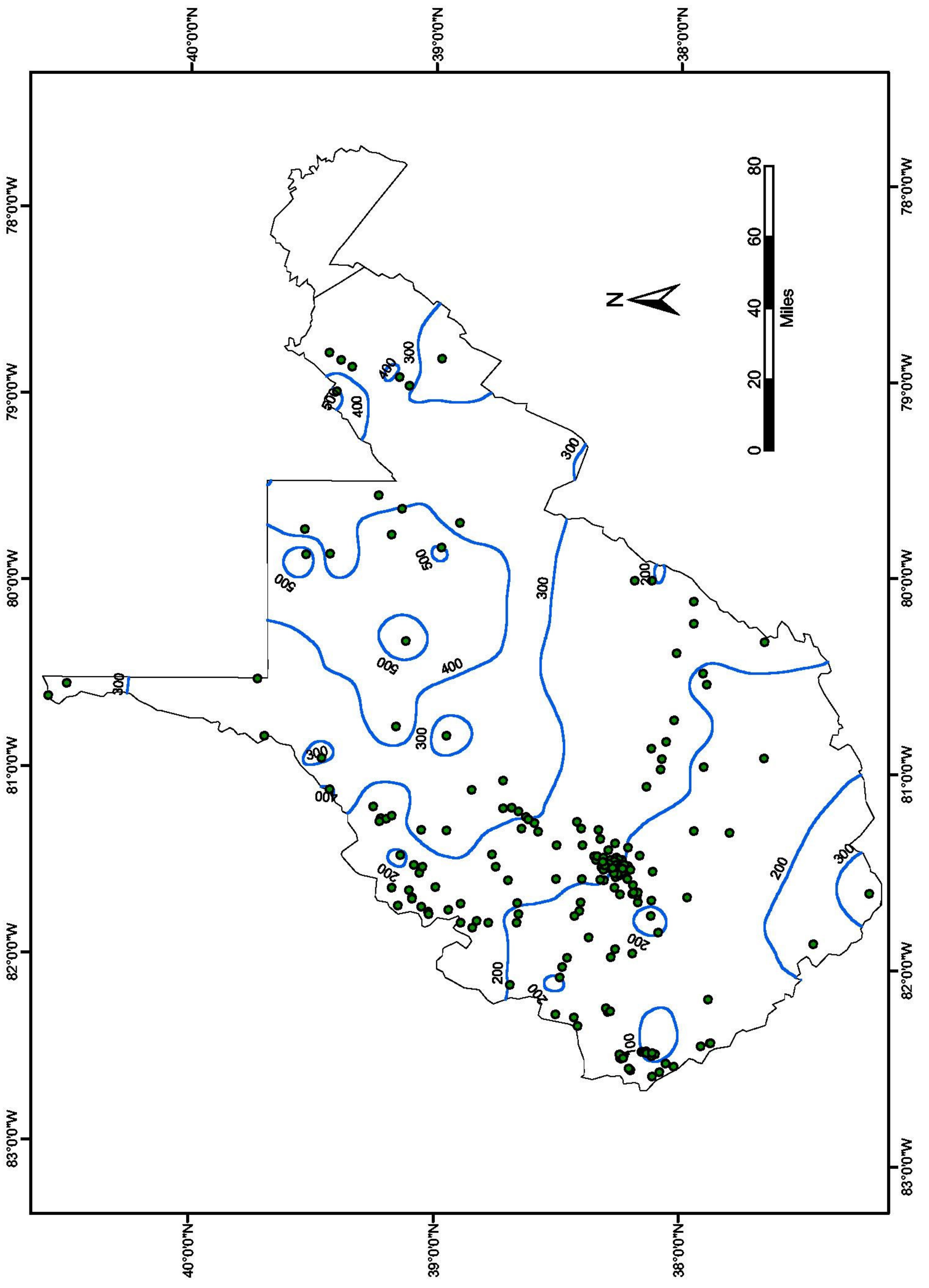

Figure M66. Contour map of thickness of Unit 4 in West Virginia

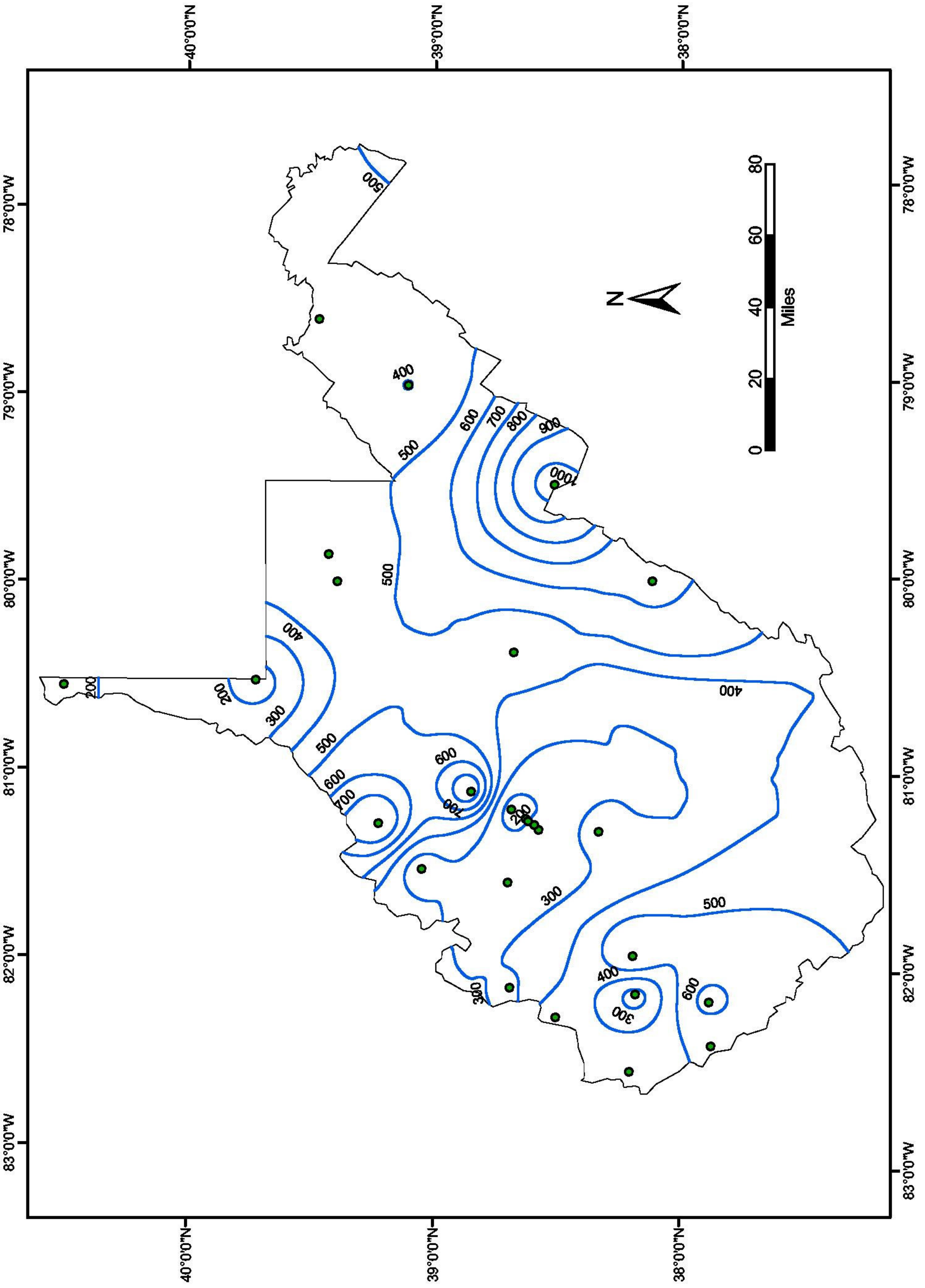

Figure M67. Contour map of thickness of Unit 5 in West Virginia

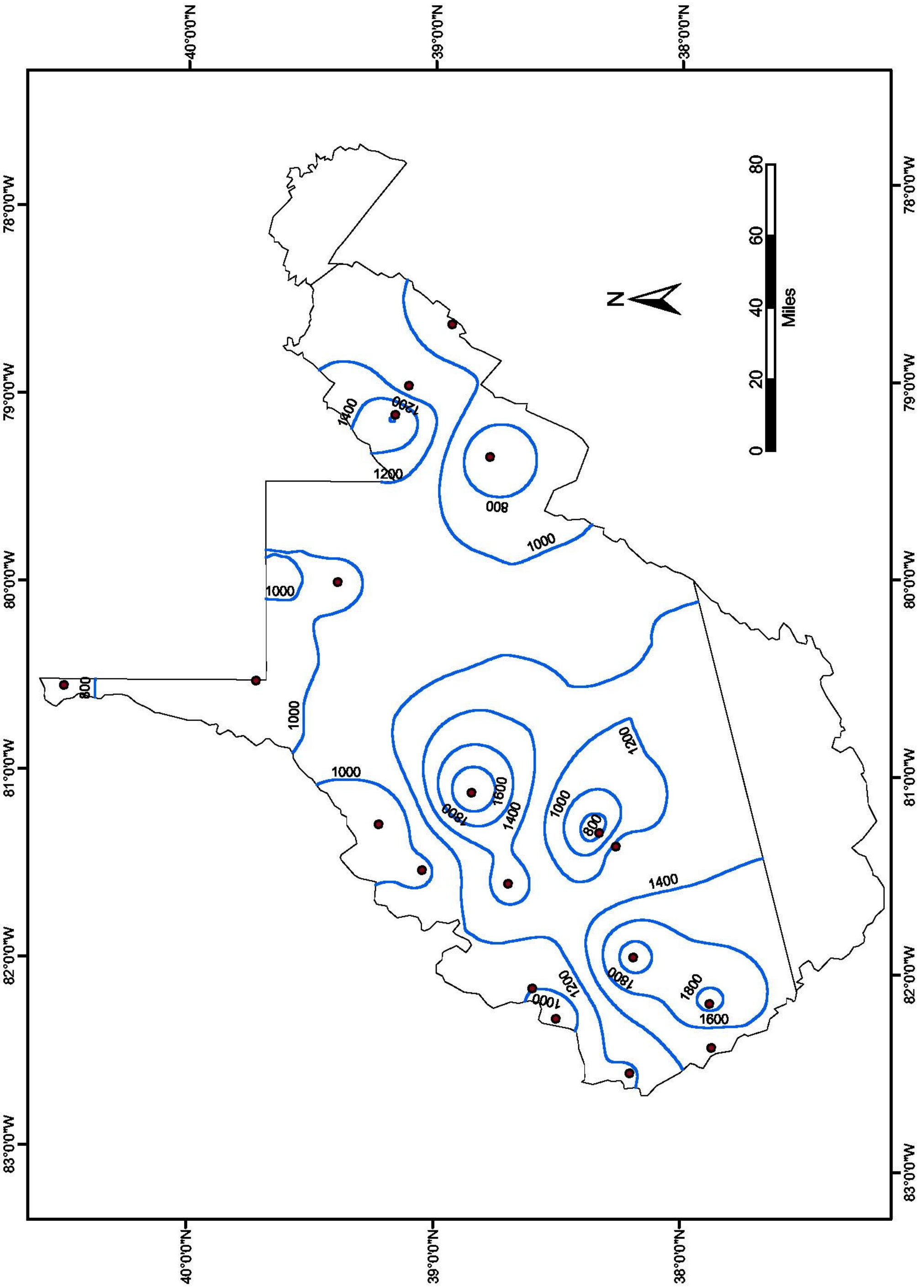

Figure M68. Contour map of thickness of Unit 6 in West Virginia

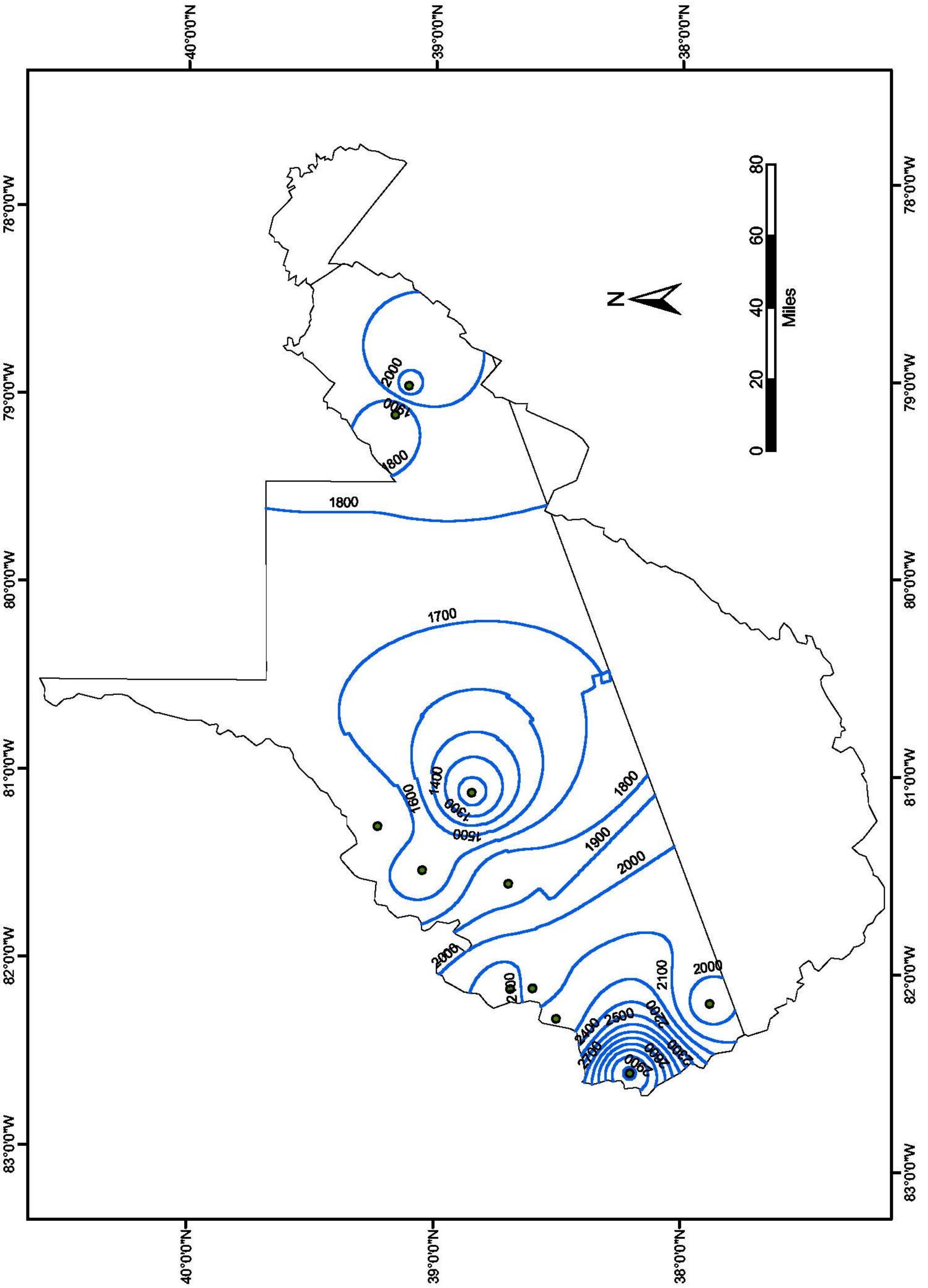

Figure M69. Contour map of thickness of Unit 7 in West Virginia

Carbonate Area Maps

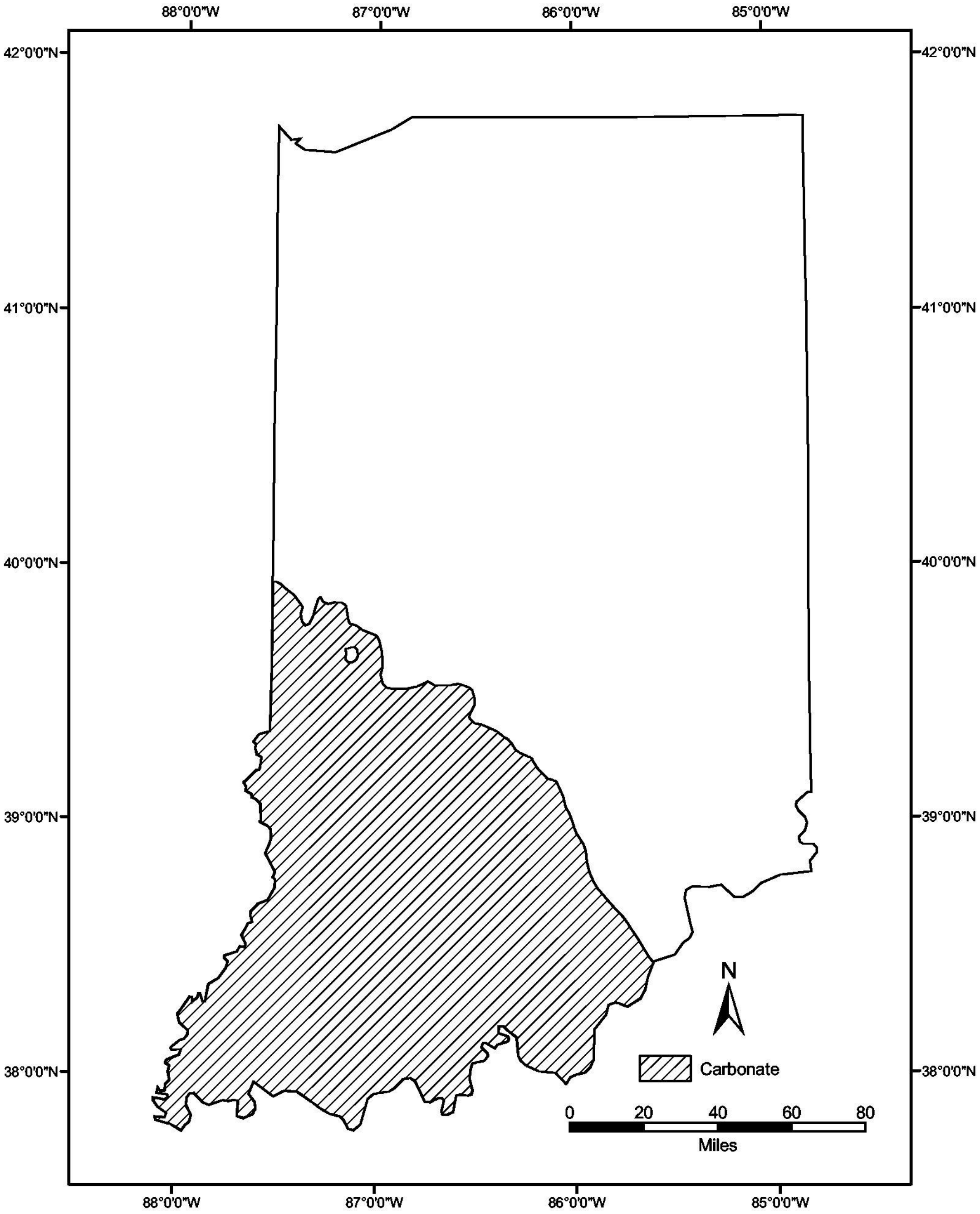

Figure M70. Carbonate areas in Indiana in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 1, 3,4,6, and 7)

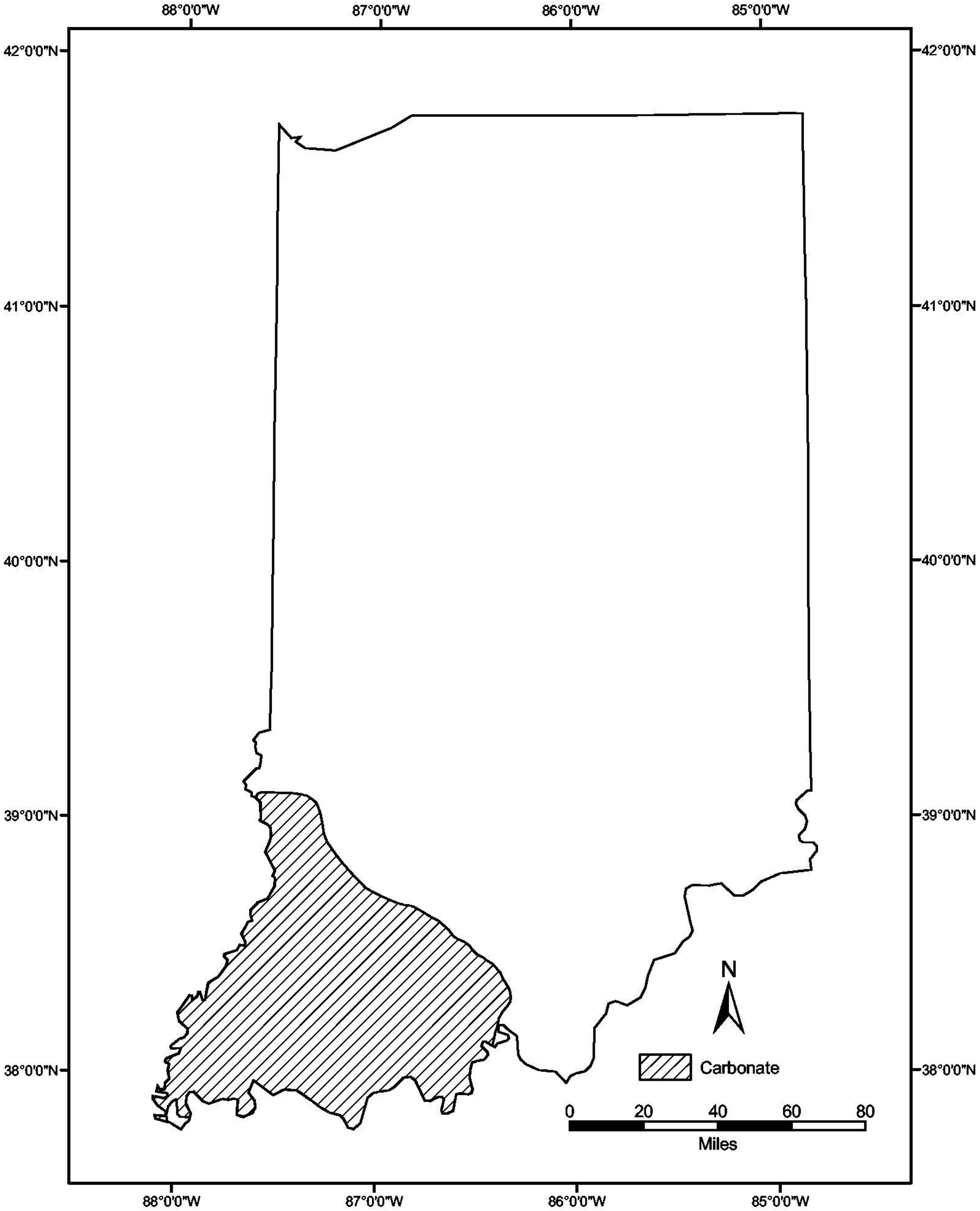

Figure M71. Carbonate areas in Indiana in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 6 and 7).

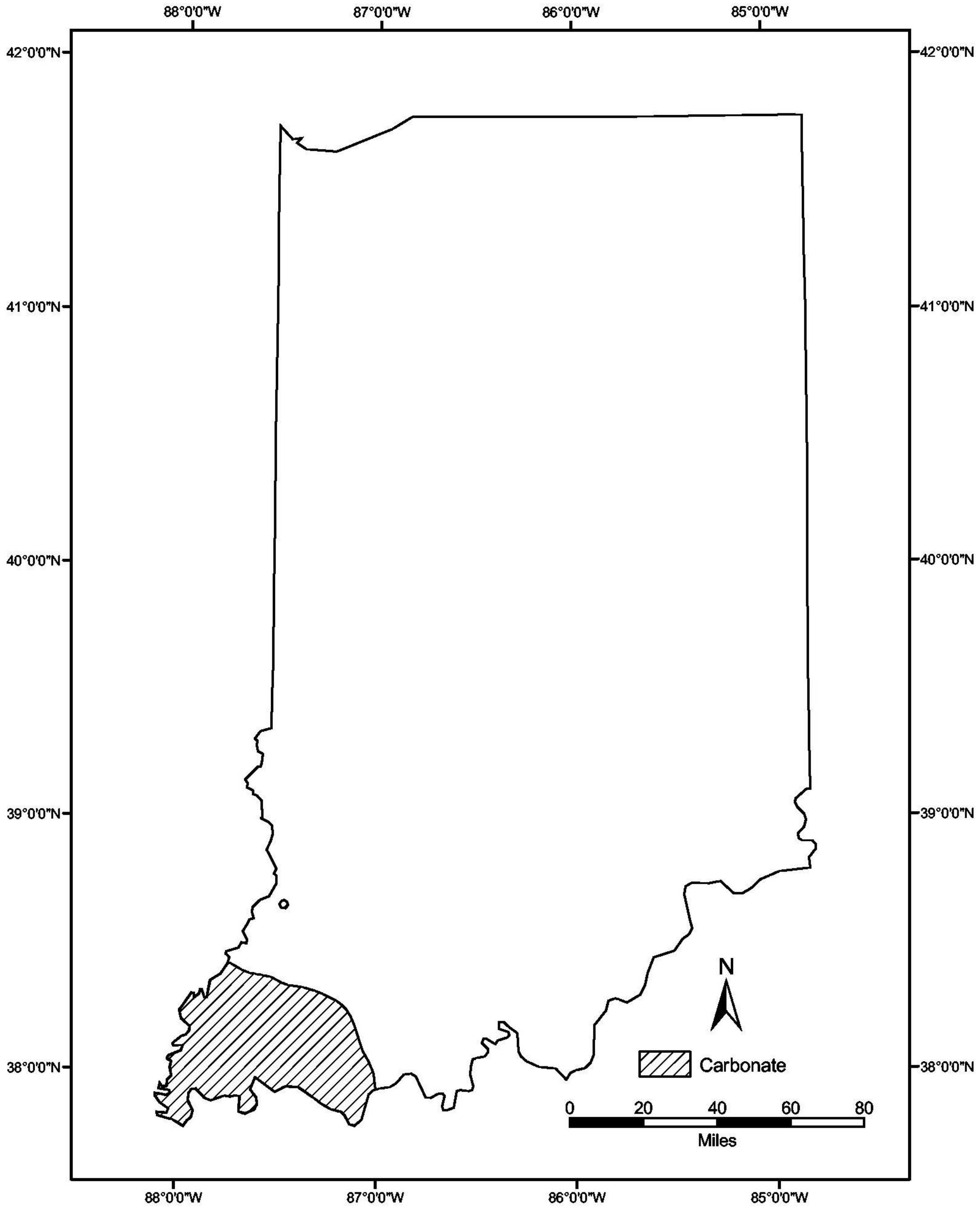

Figure M72. Carbonate areas in Indiana in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Unit 7).

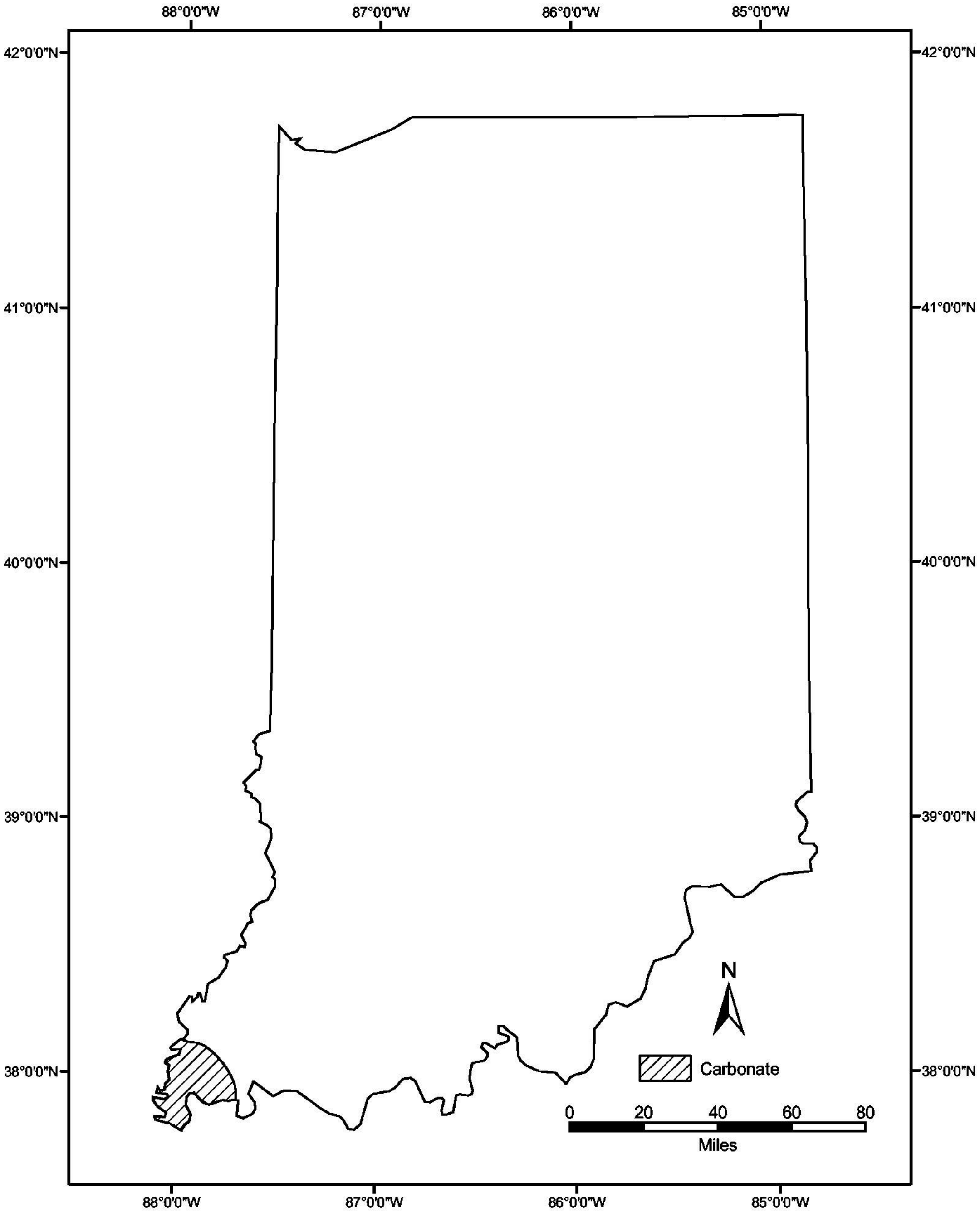

Figure M73. Carbonate areas in Indiana in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Unit 7).

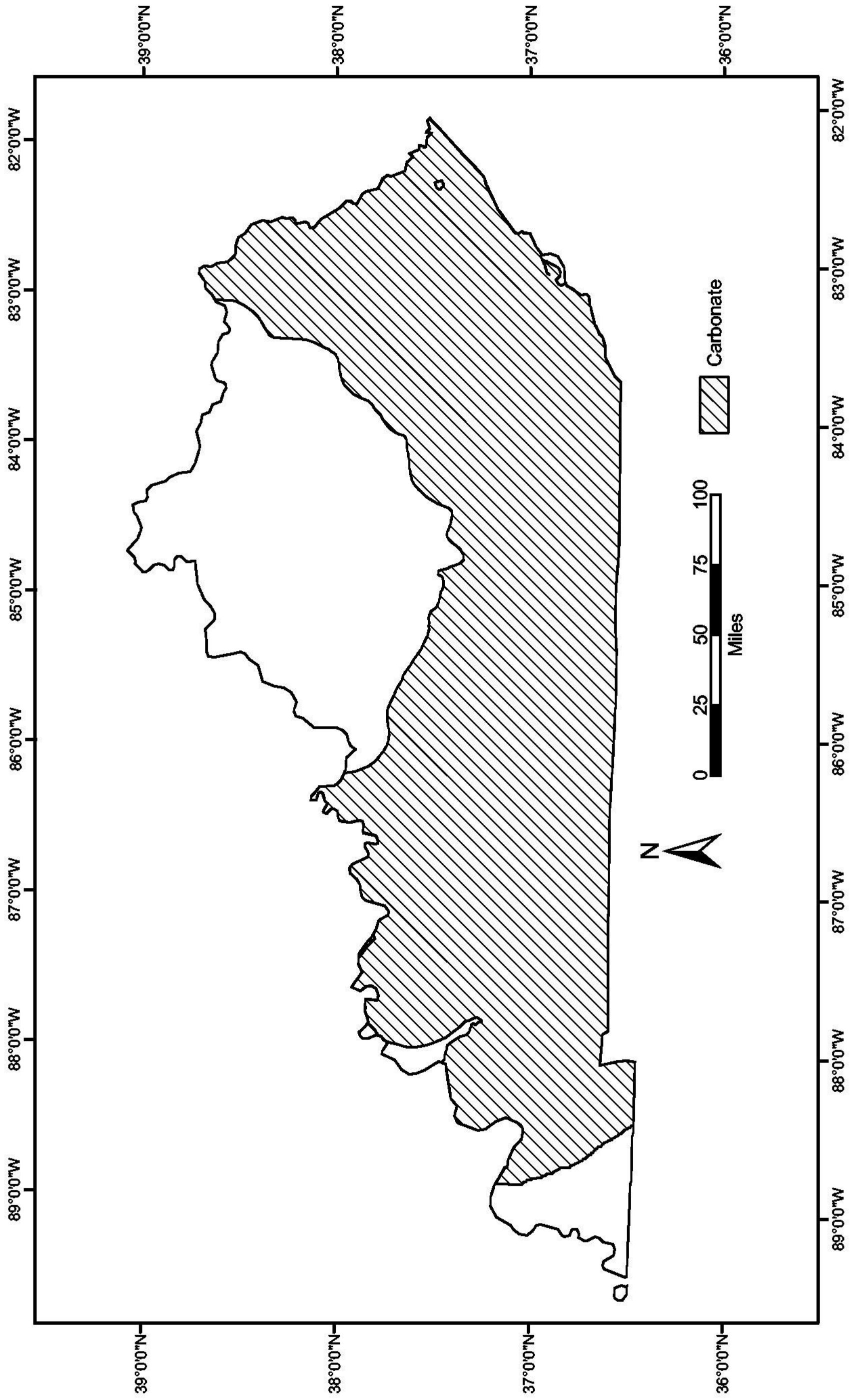

Figure M74. Carbonate areas in Kentucky in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 4, 5, 6, and 7).

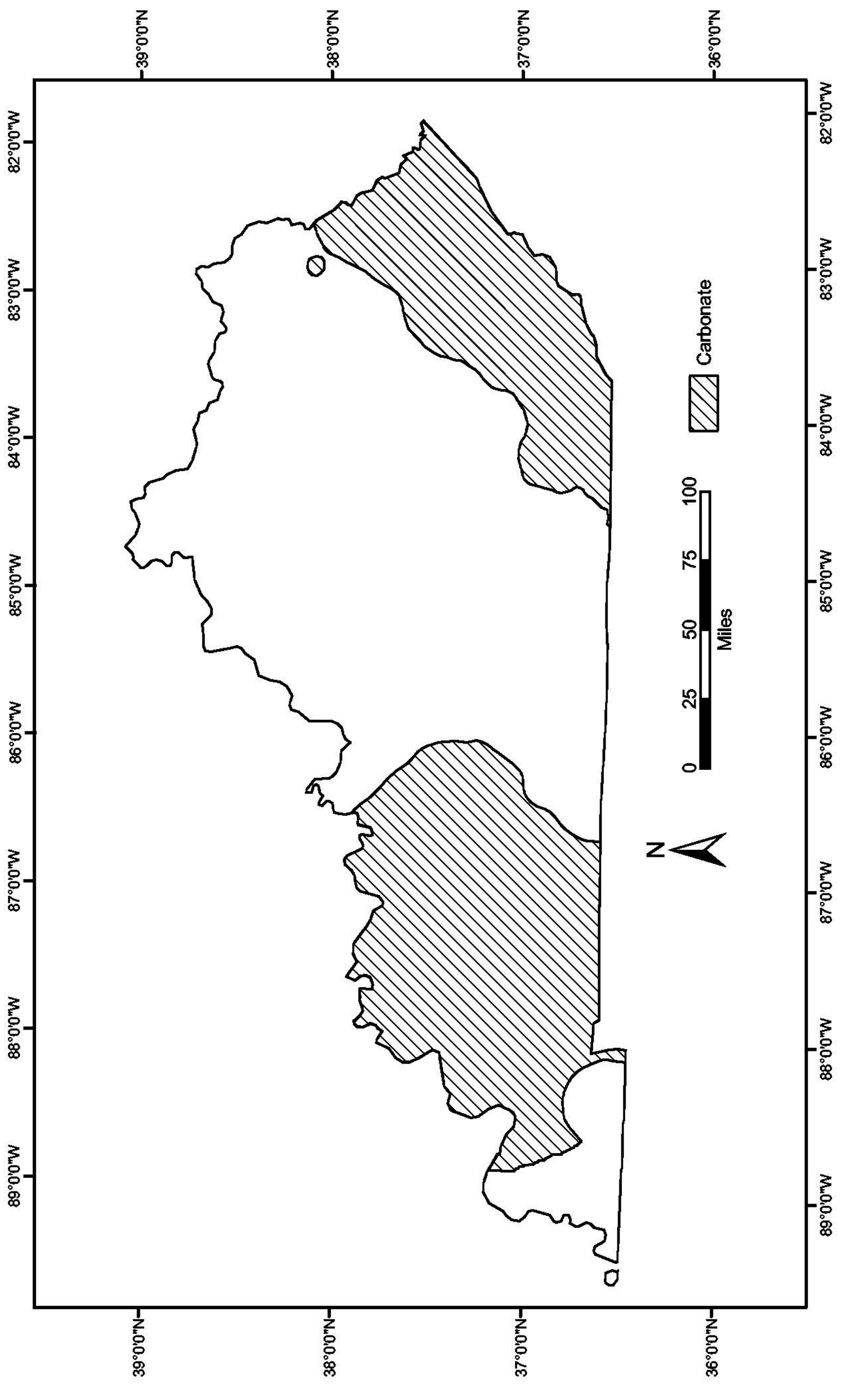

Figure M75. Carbonate areas in Kentucky in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 5, 6, and 7).

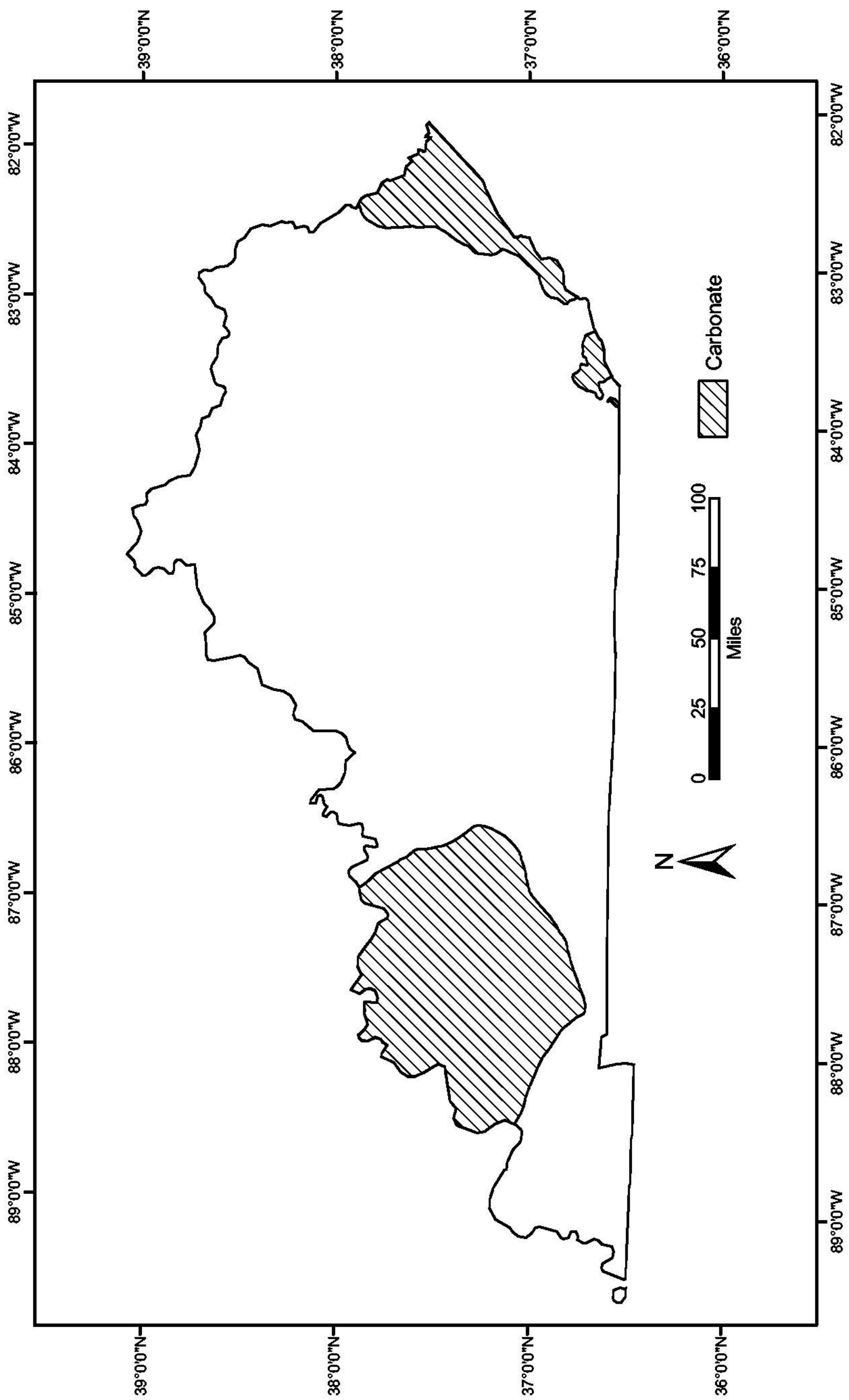

Figure M76. Carbonate areas in Kentucky in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Unit 7).

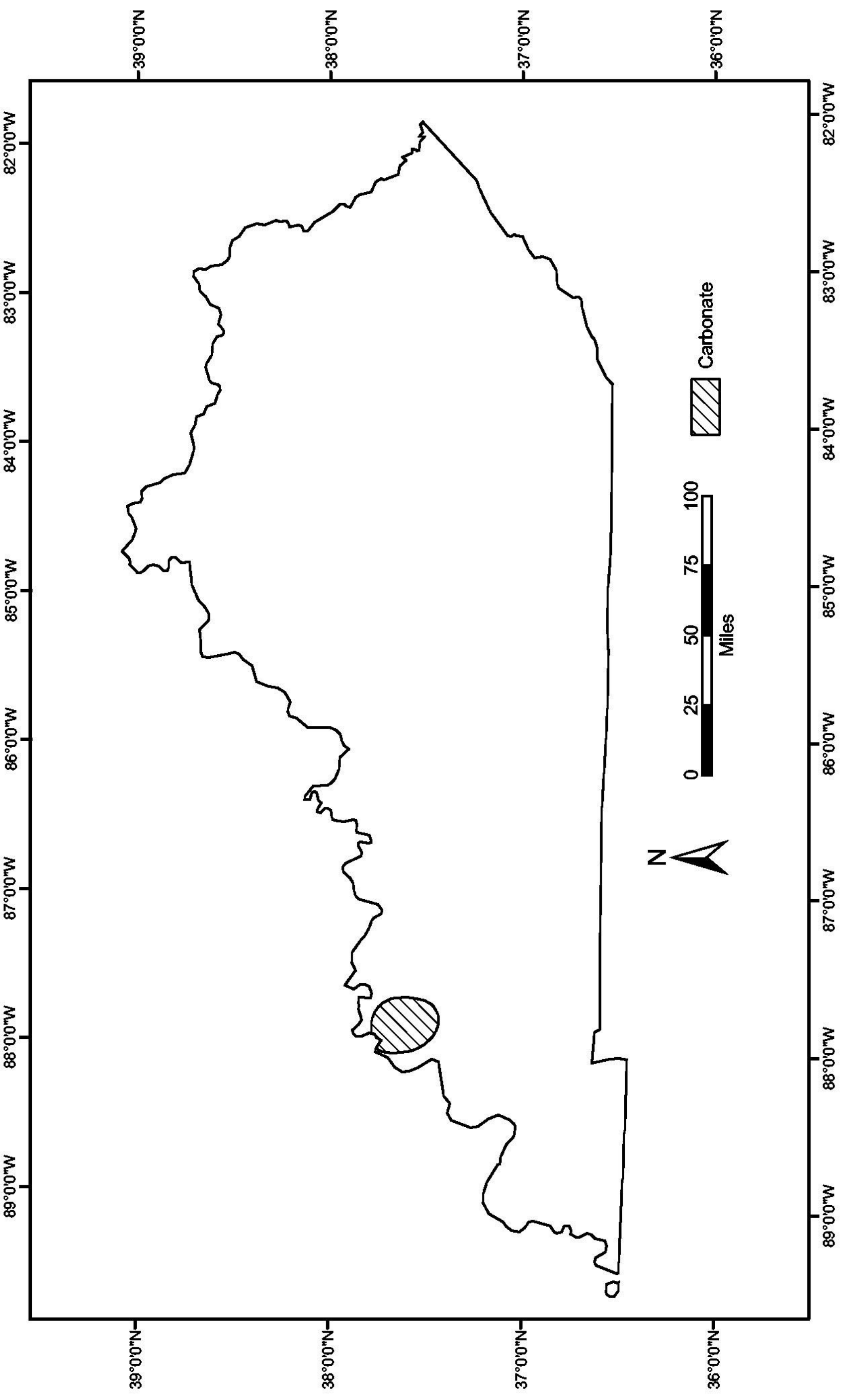

Figure M77. Carbonate areas in Kentucky in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Unit 7).

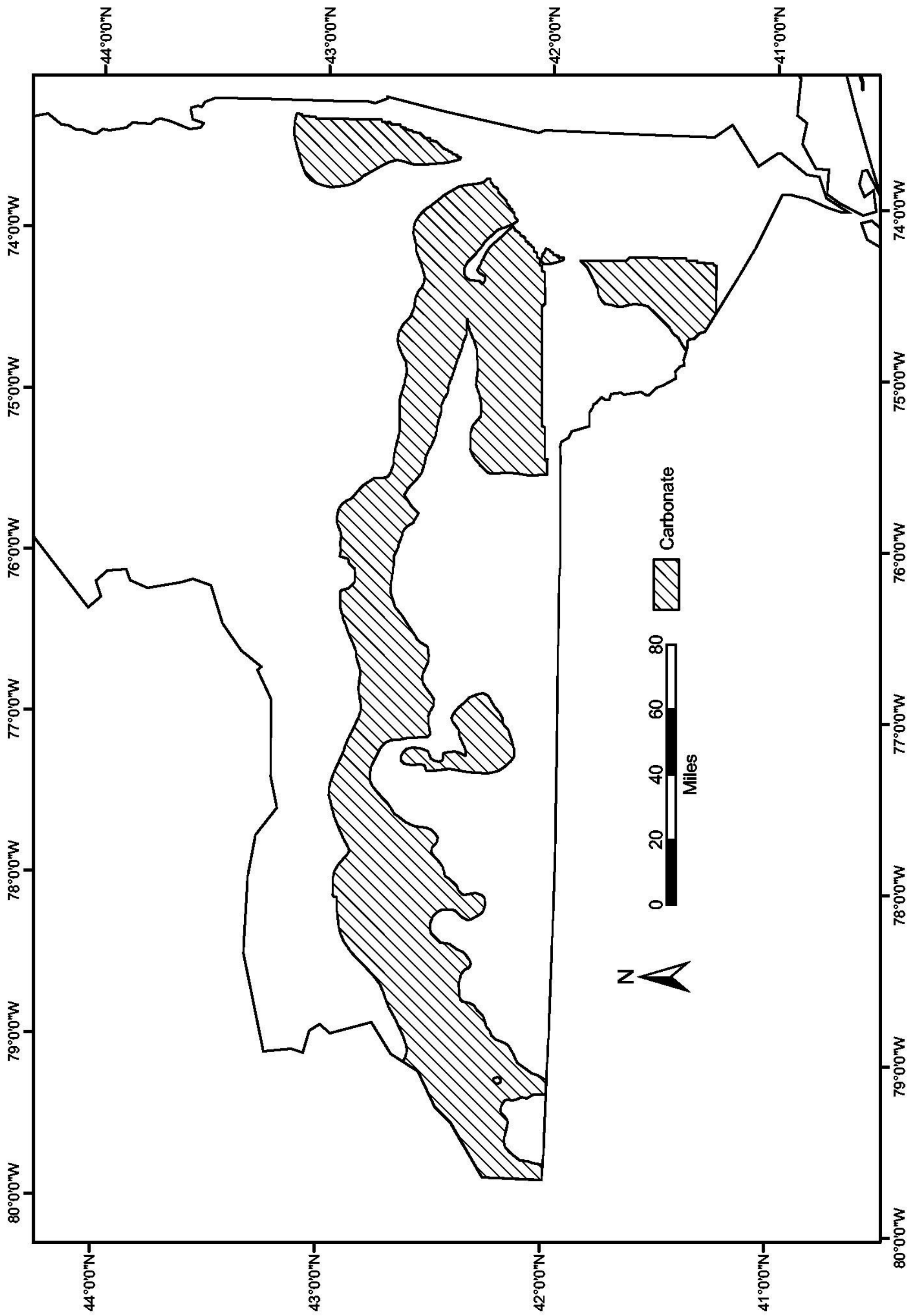

Figure M78. Carbonate areas in New York in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6, and 7).

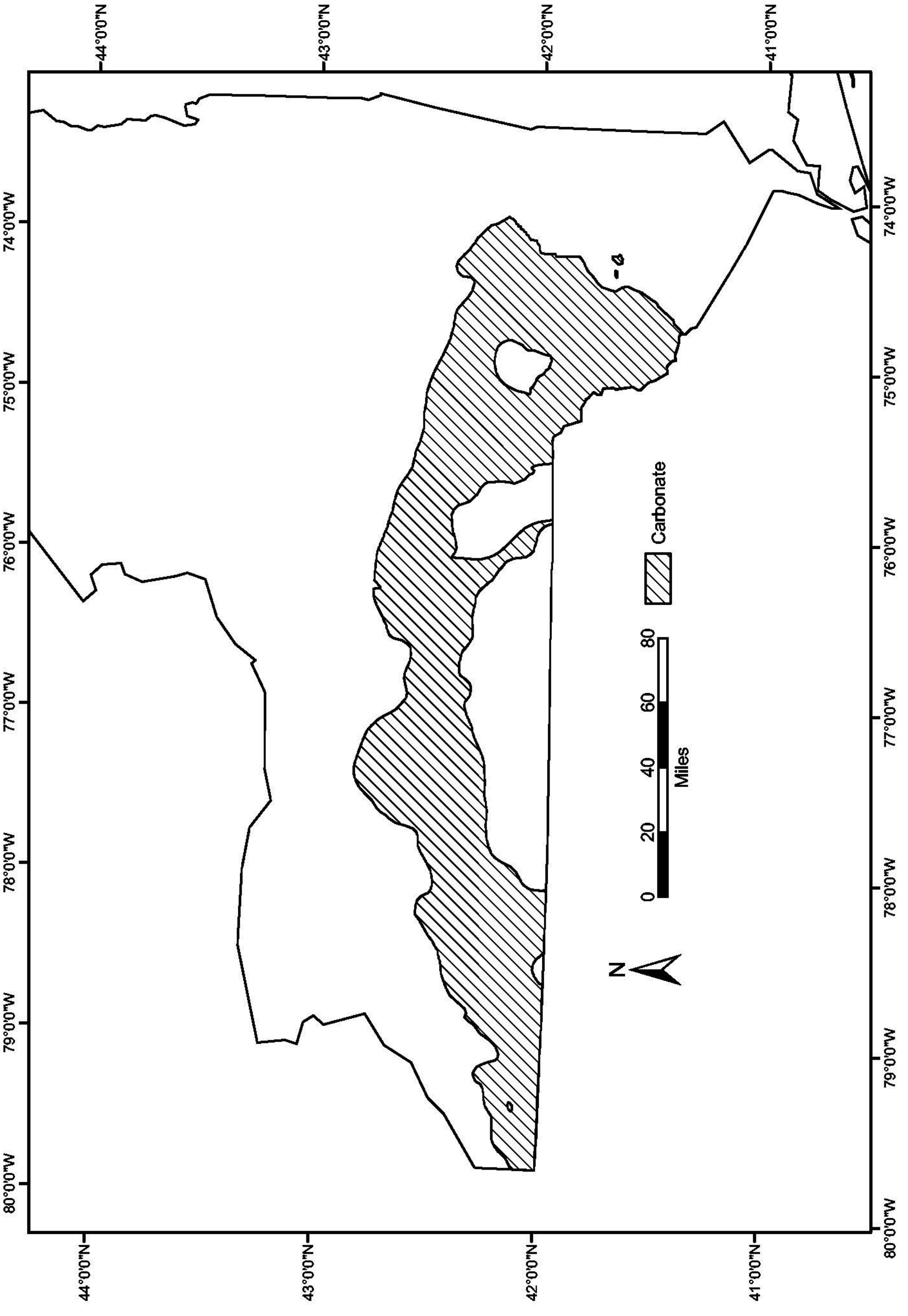

Figure M79. Carbonate areas in New York in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 5, 6, and 7).

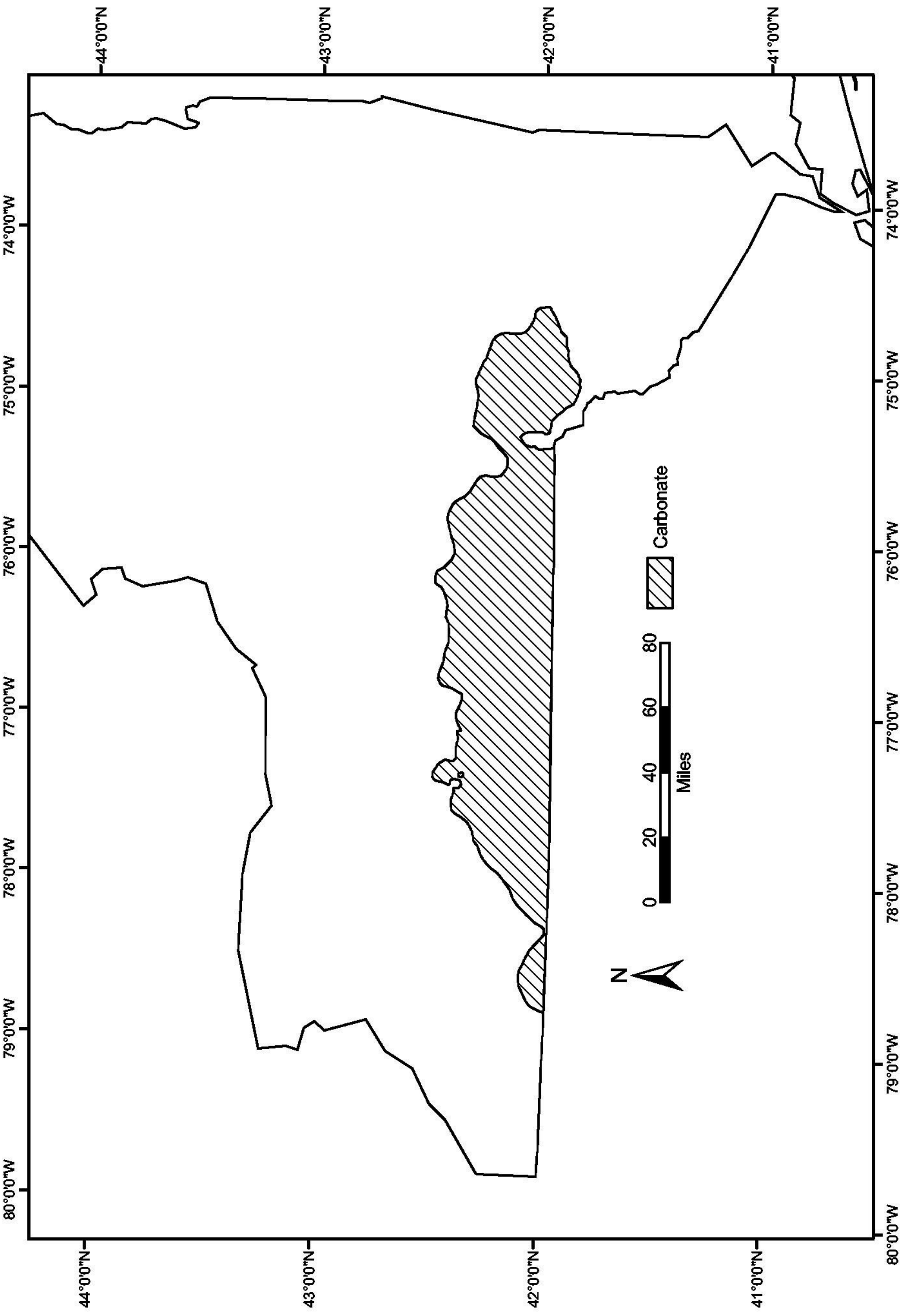

Figure M80. Carbonate areas in New York in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 5, 6, and 7).

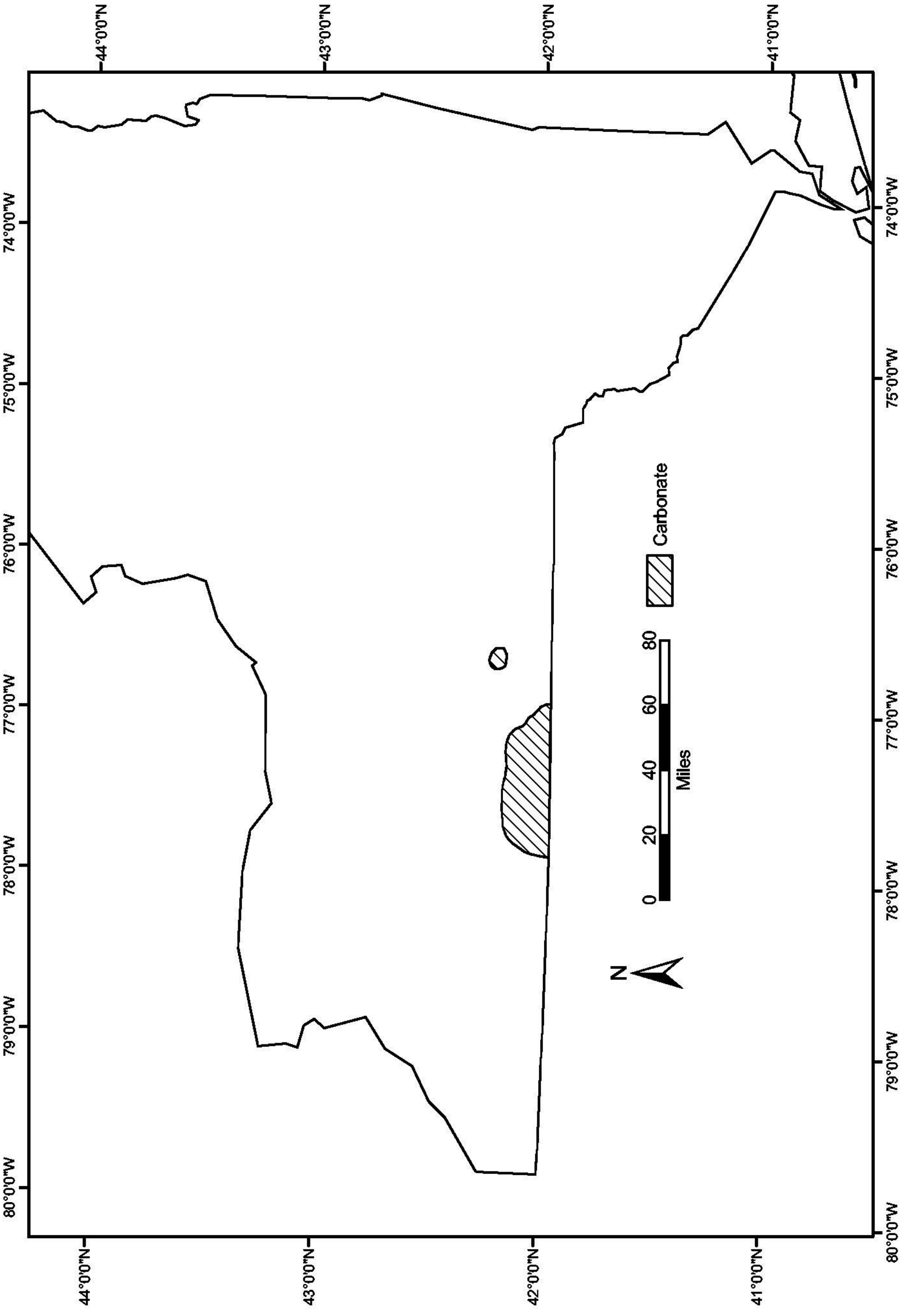

Figure M81. Carbonate areas in New York in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Units 6 and 7).

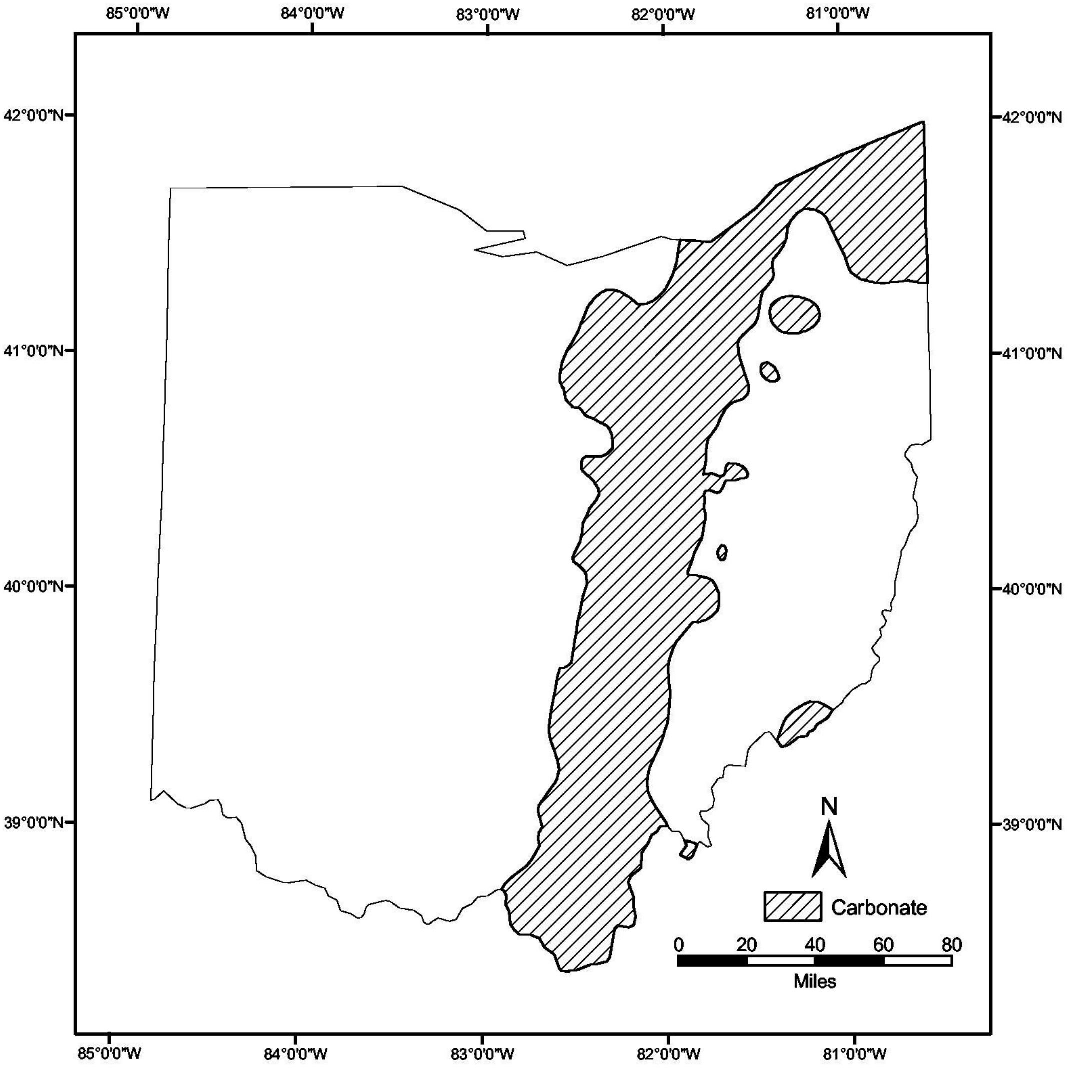

Figure M82. Carbonate areas in Ohio in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 6 and 7).

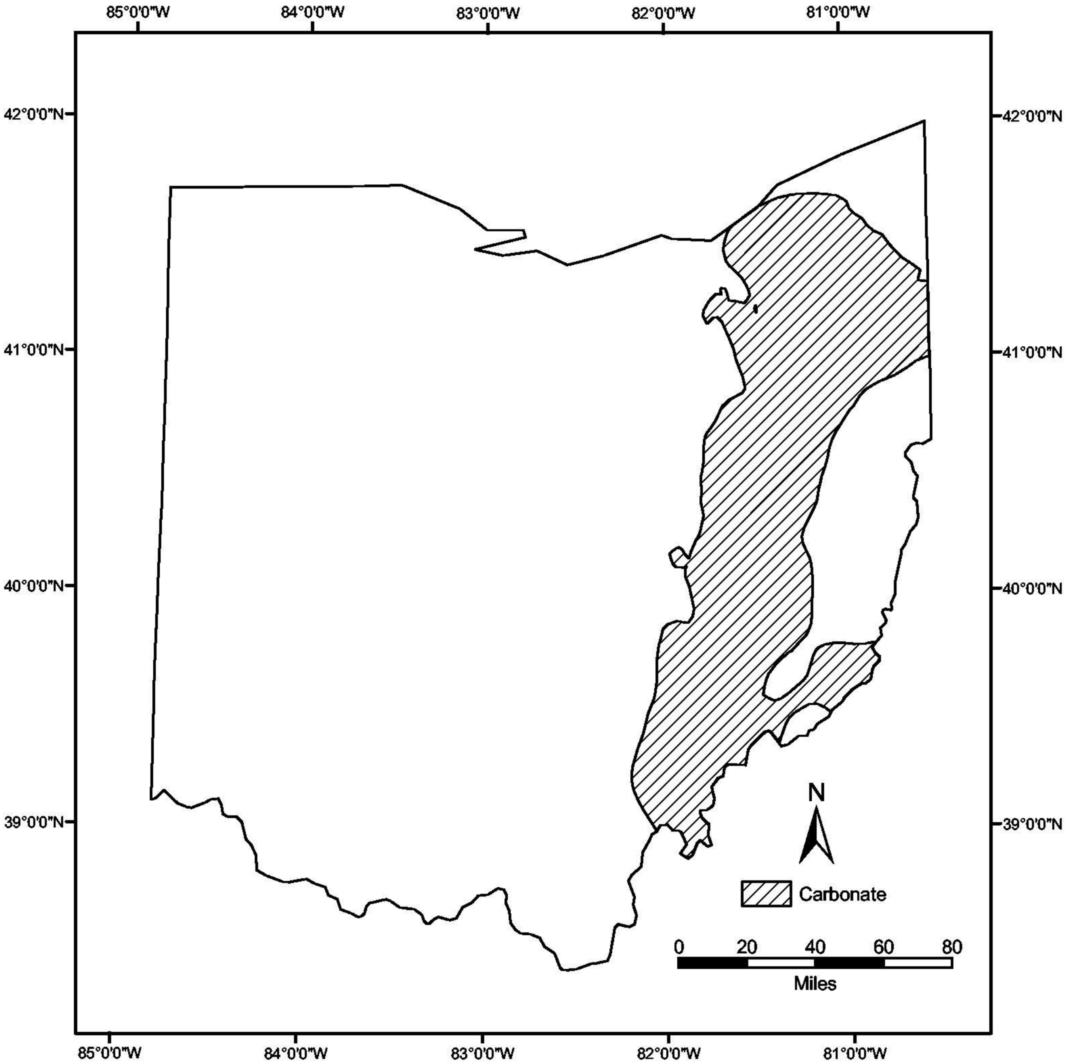

Figure M83. Carbonate areas in Ohio in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 6 and 7).

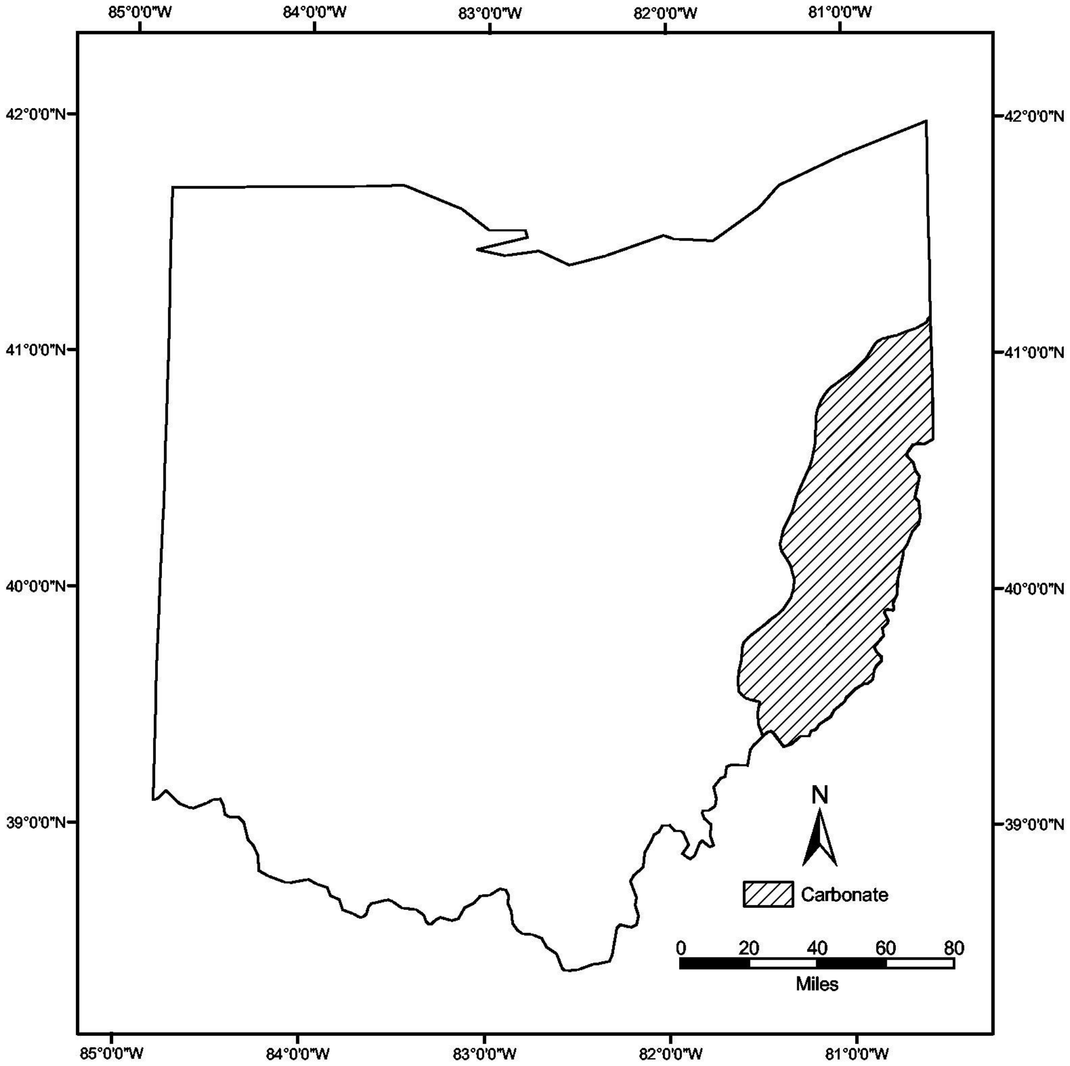

Figure M84. Carbonate areas in Ohio in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 6 and 7).

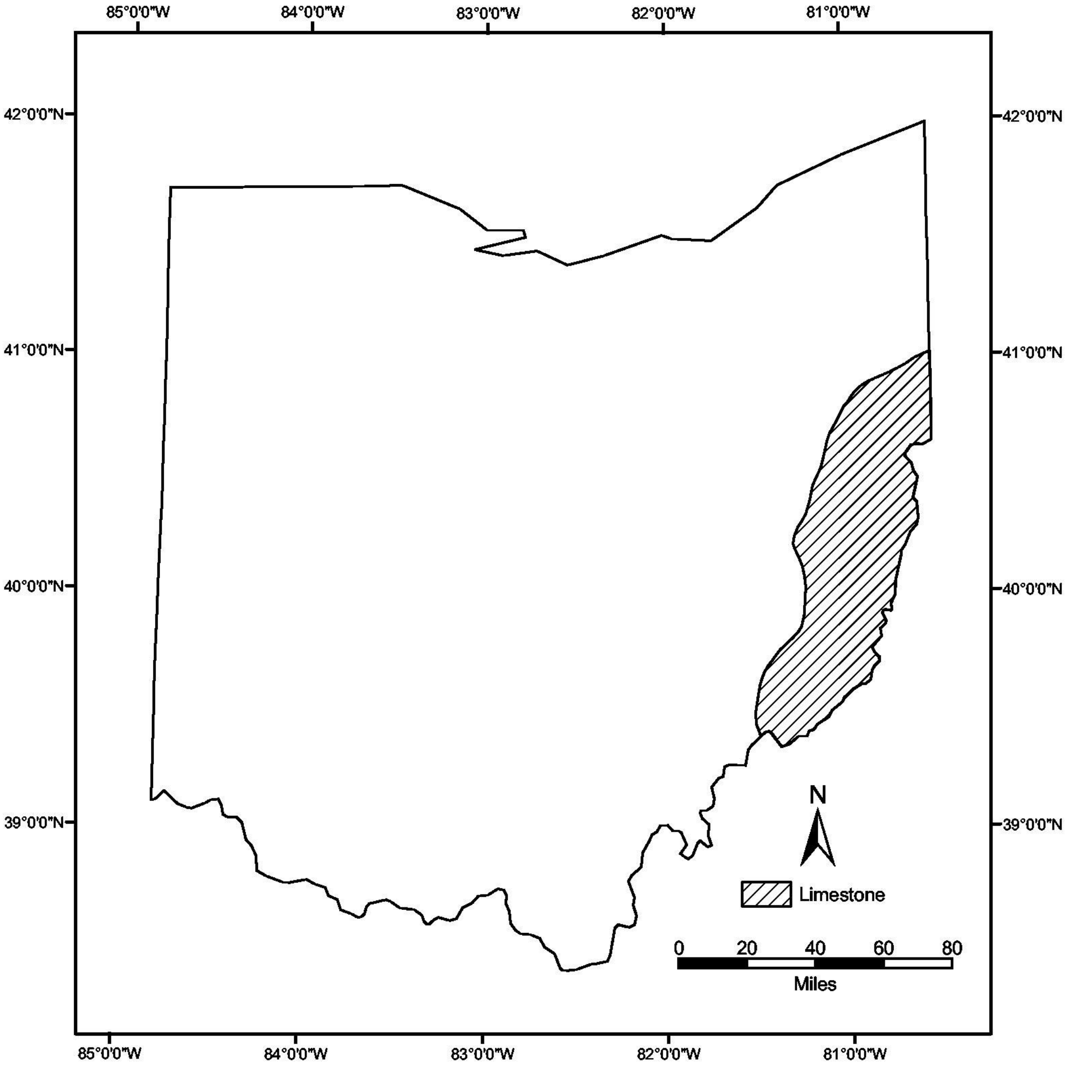

Figure M85. Limestone areas in Ohio in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Unit 6).

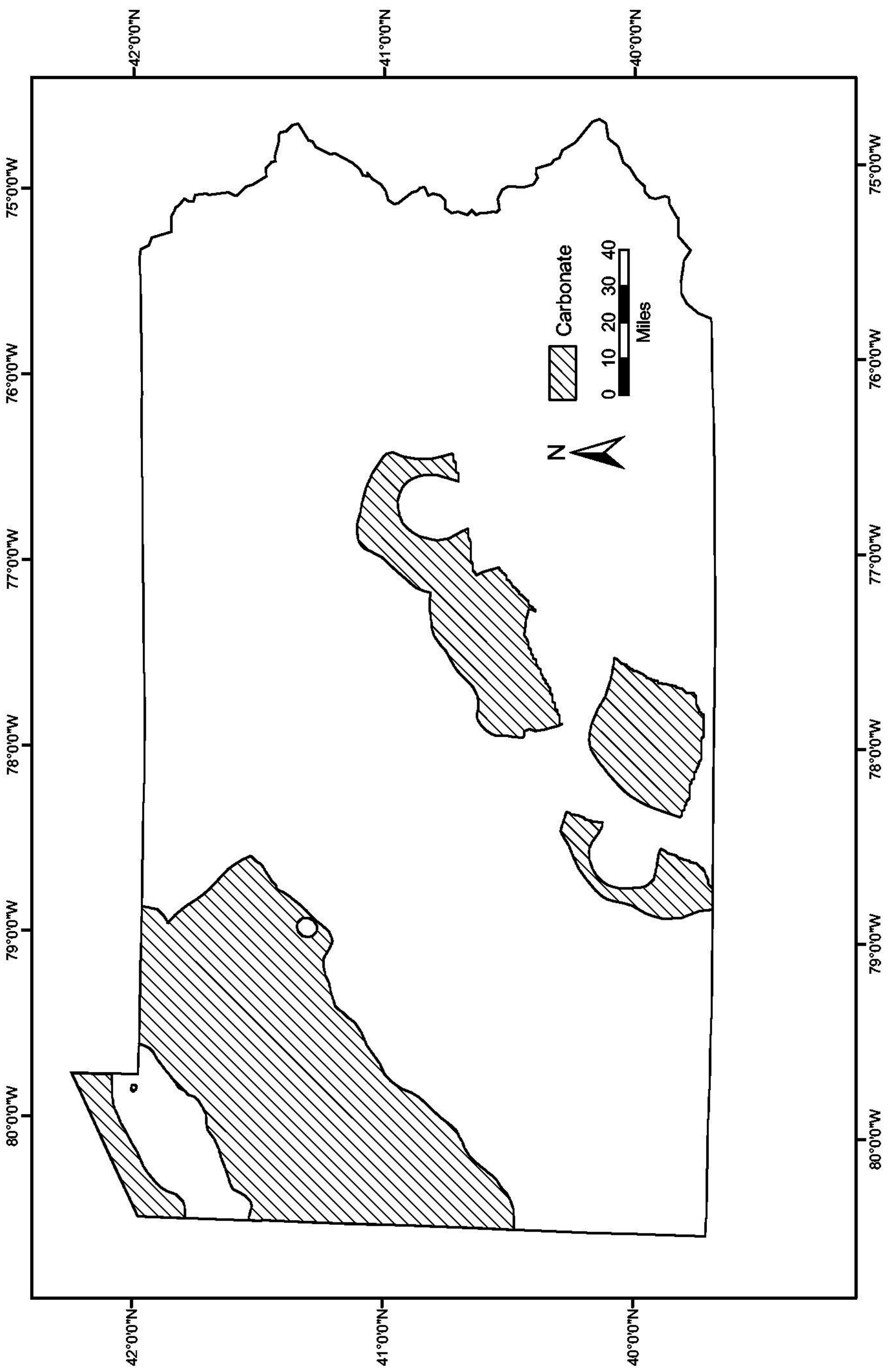

Figure M86. Carbonate areas in Pennsylvania in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6 and 7).

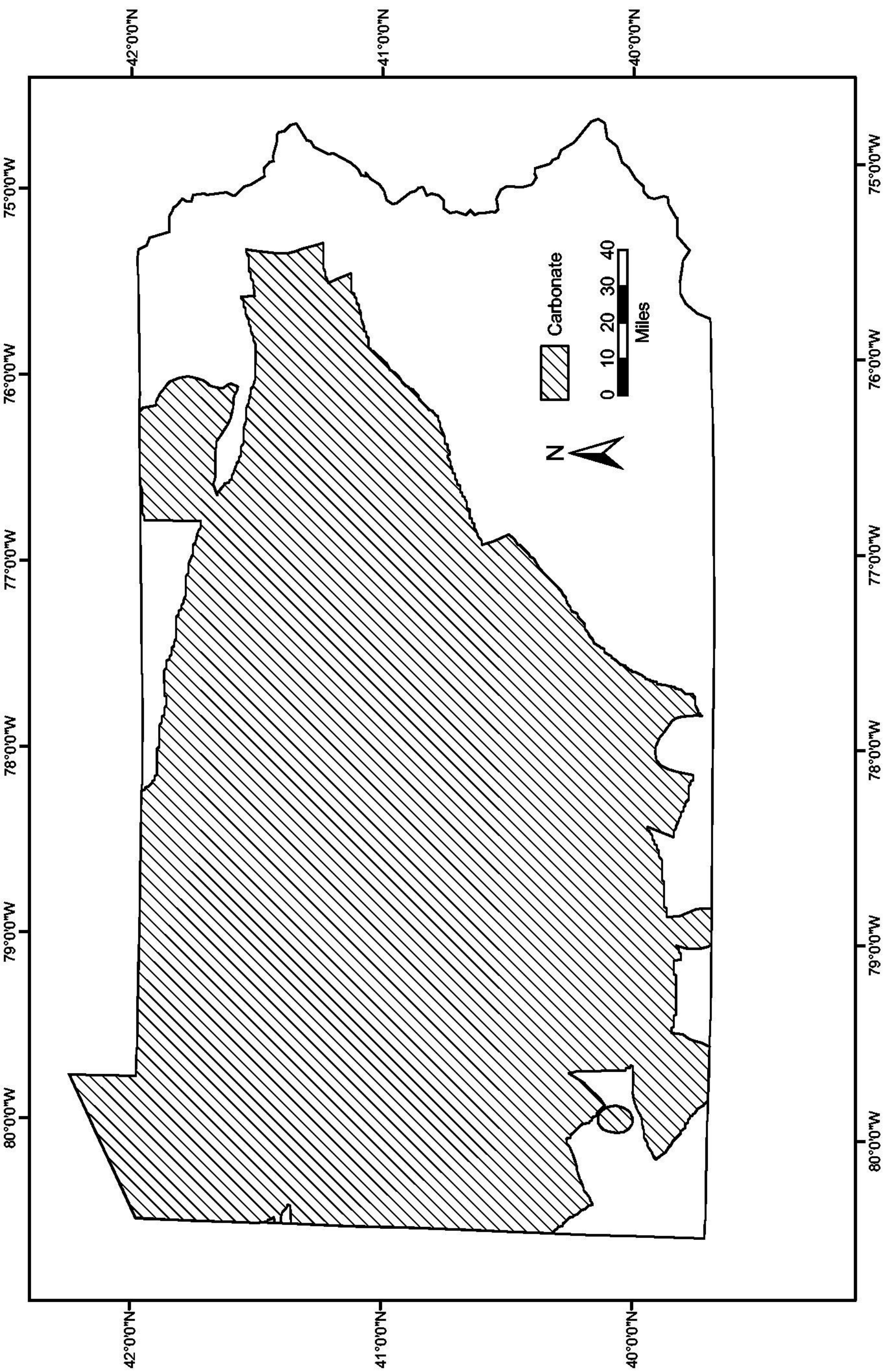

Figure M87. Carbonate areas in Pennsylvania in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 2, 3, 4, 5, 6 and 7).

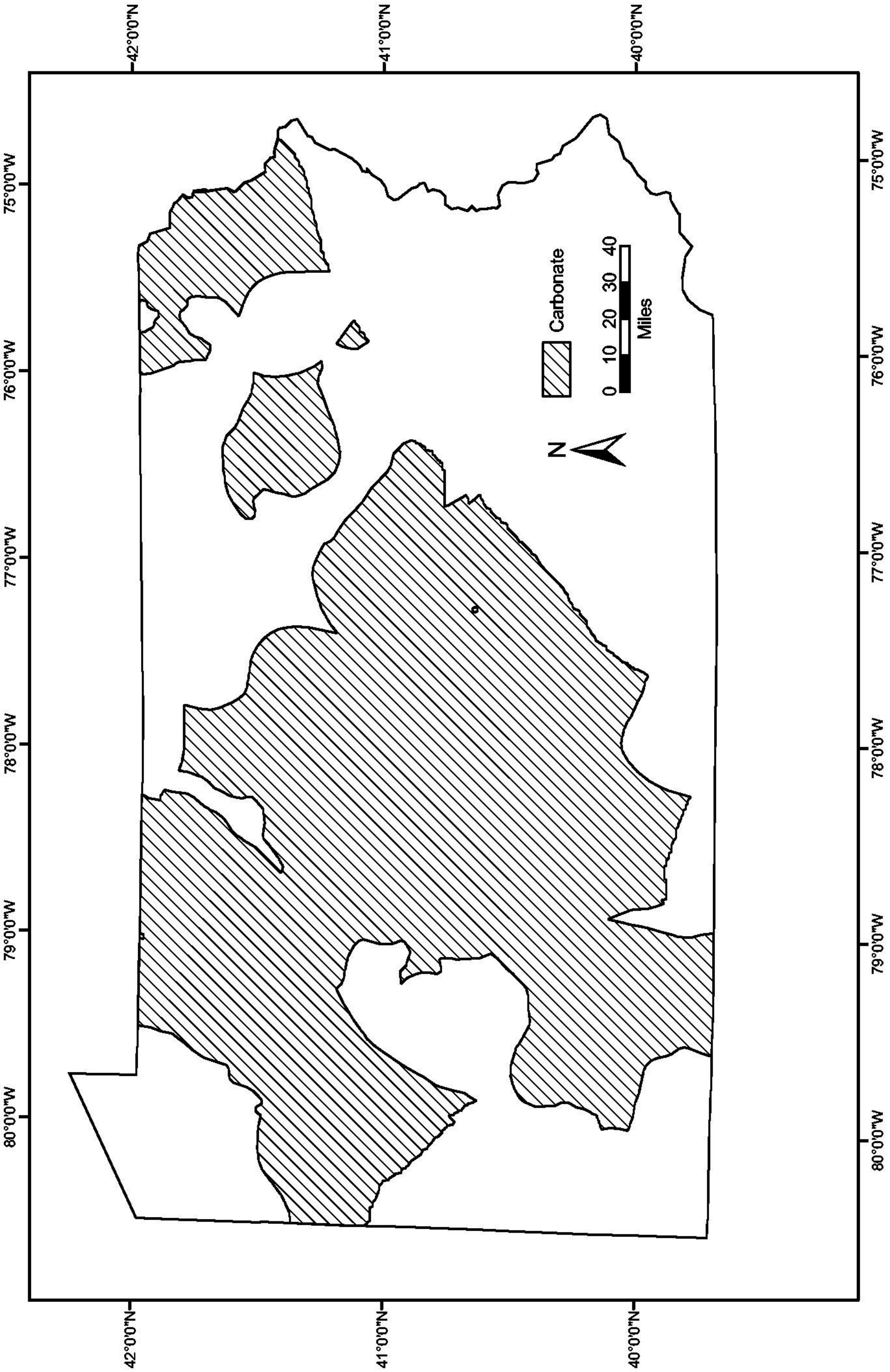

Figure M88. Carbonate areas in Pennsylvania in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6 and 7).

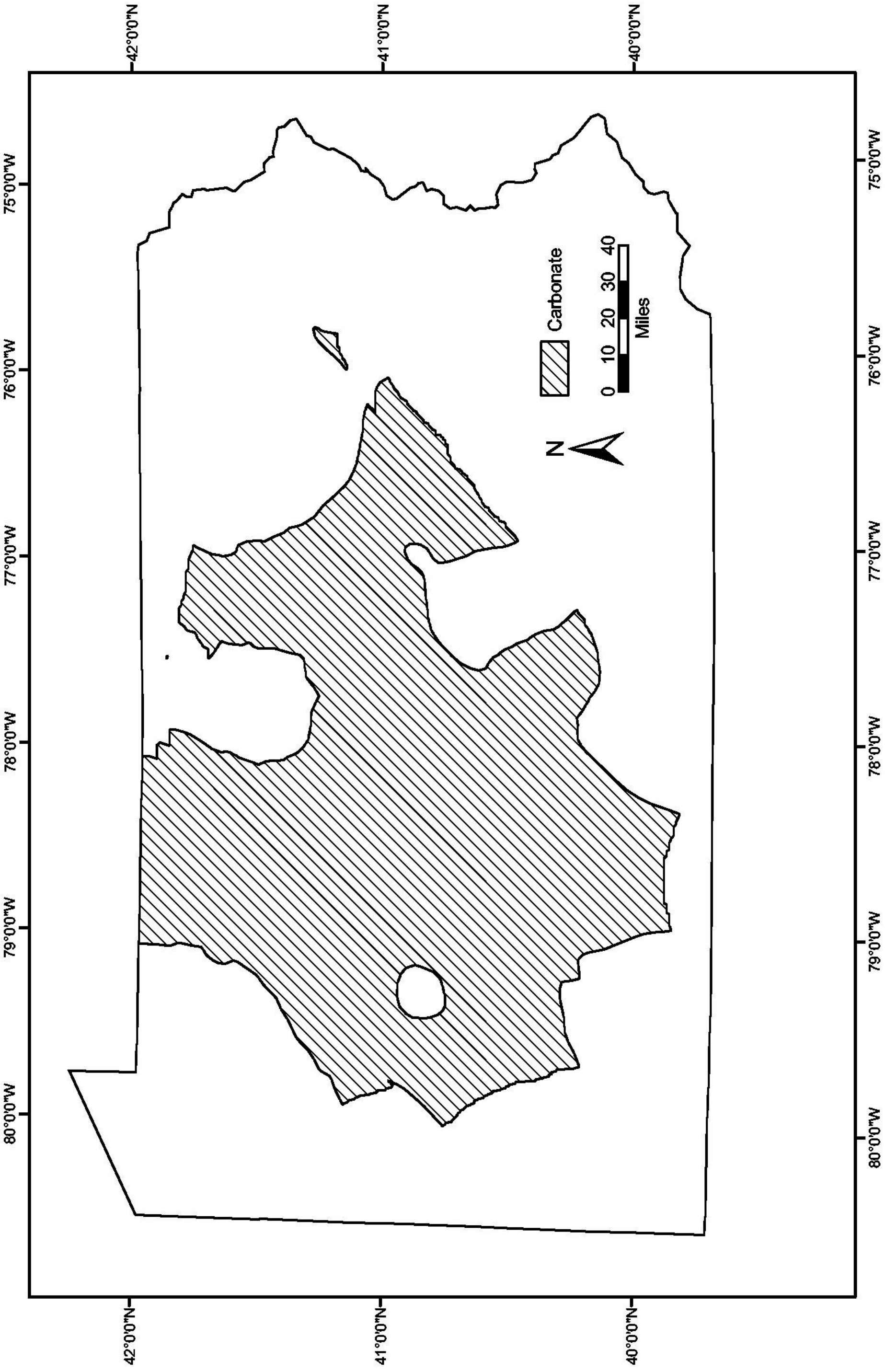

Figure M89. Carbonate areas in Pennsylvania in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Units 5, 6 and 7).

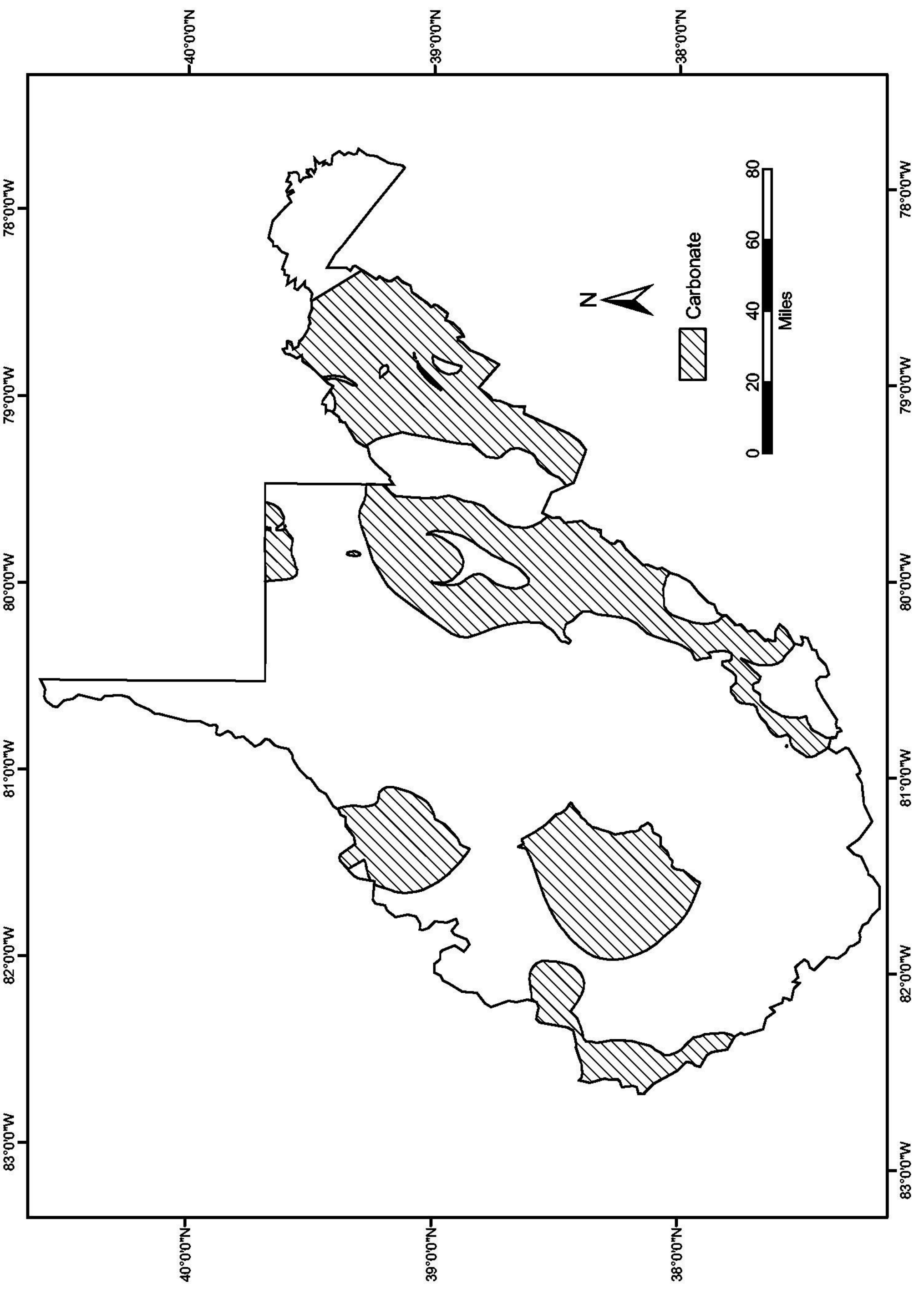

Figure M90. Carbonate areas in West Virginia in the 4000 ft to 60000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6 and 7).

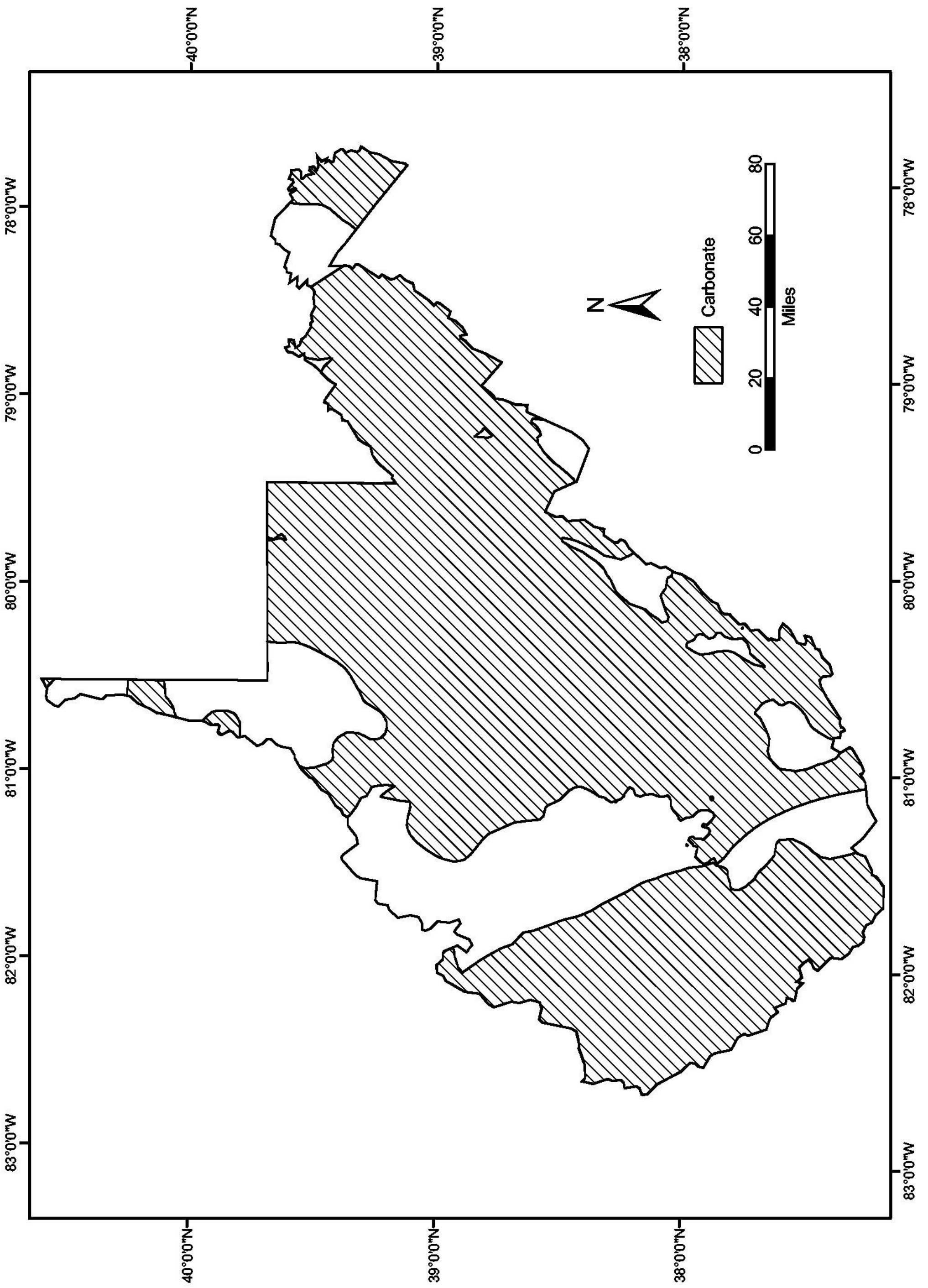

Figure M91. Carbonate areas in West Virginia in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6 and 7).

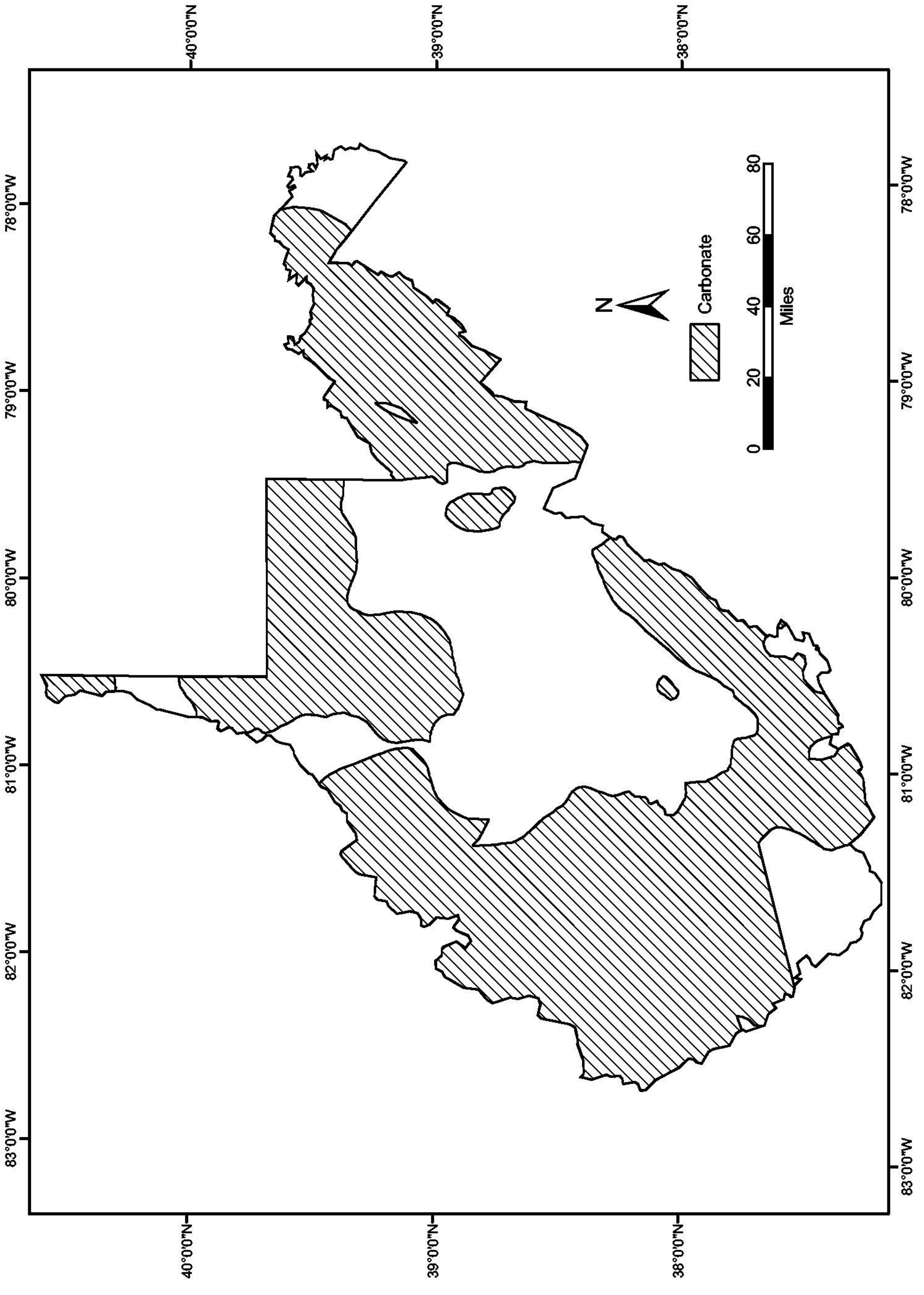

Figure M92. Carbonate areas in West Virginia in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 3, 4, 5, 6 and 7).

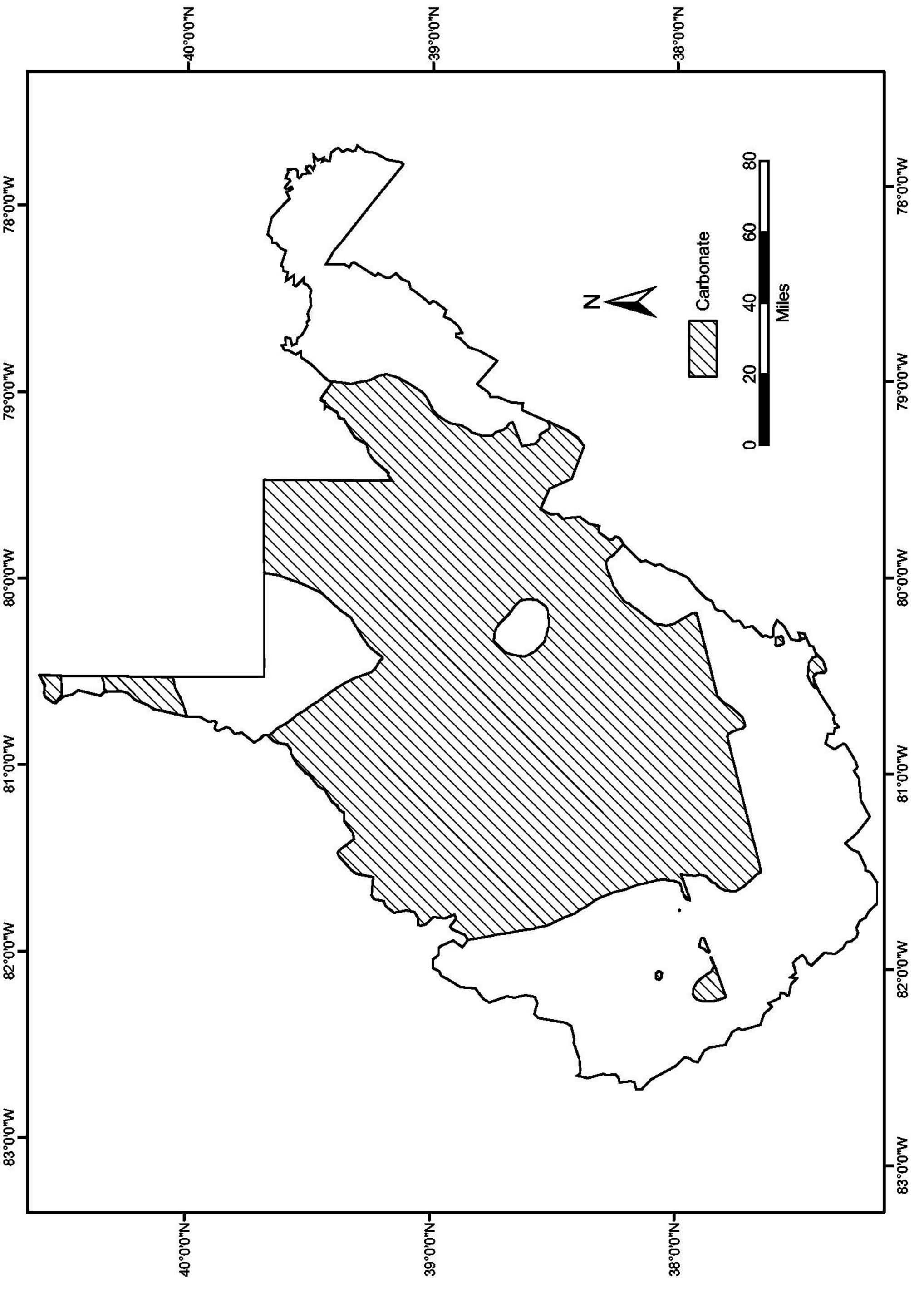

Figure M93. Carbonate areas in West Virginia in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Units 4, 5, 6 and 7).

Limestone Area Maps

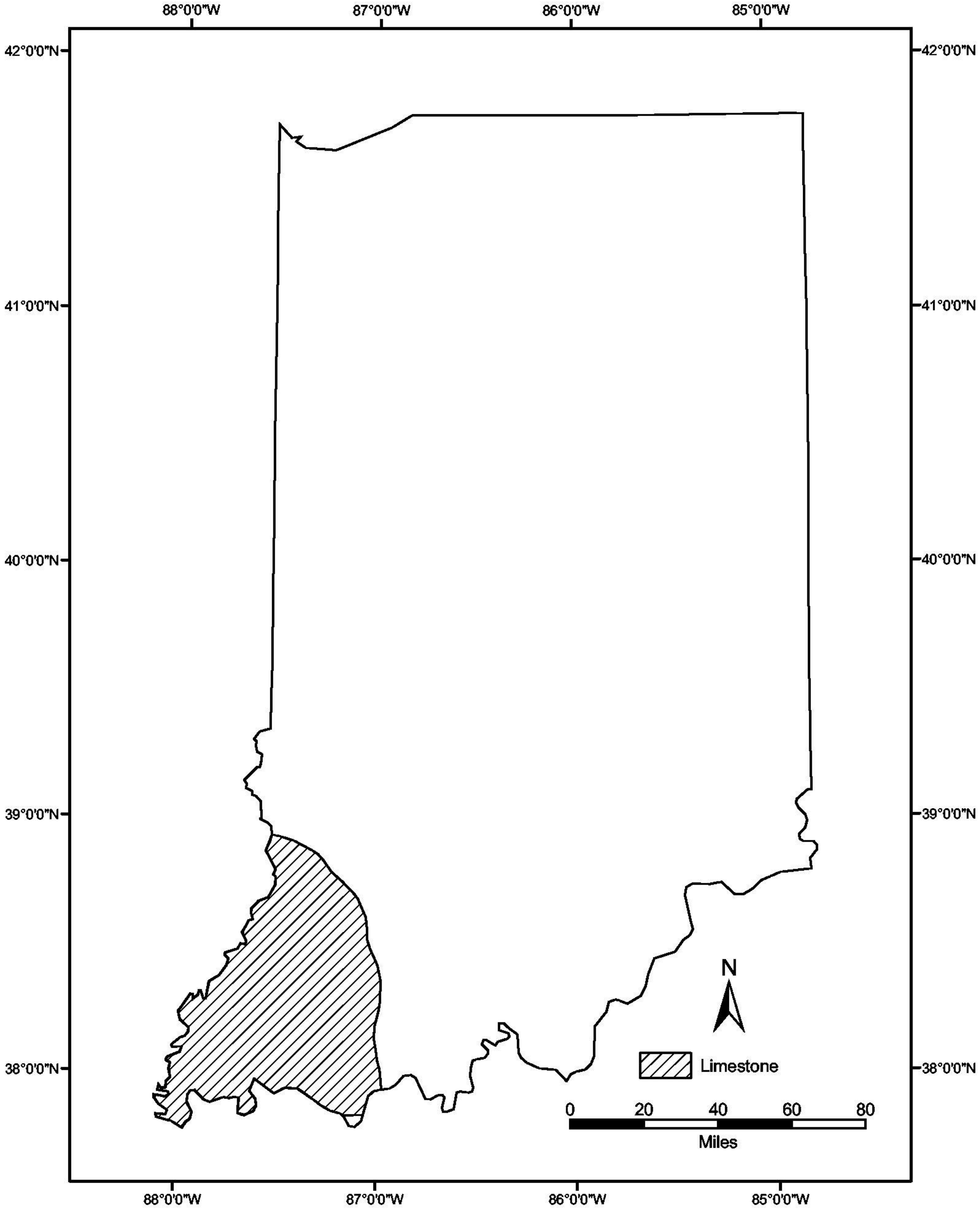

Figure M94. Limestone areas in Indiana in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 1, 3, 4, and 6).

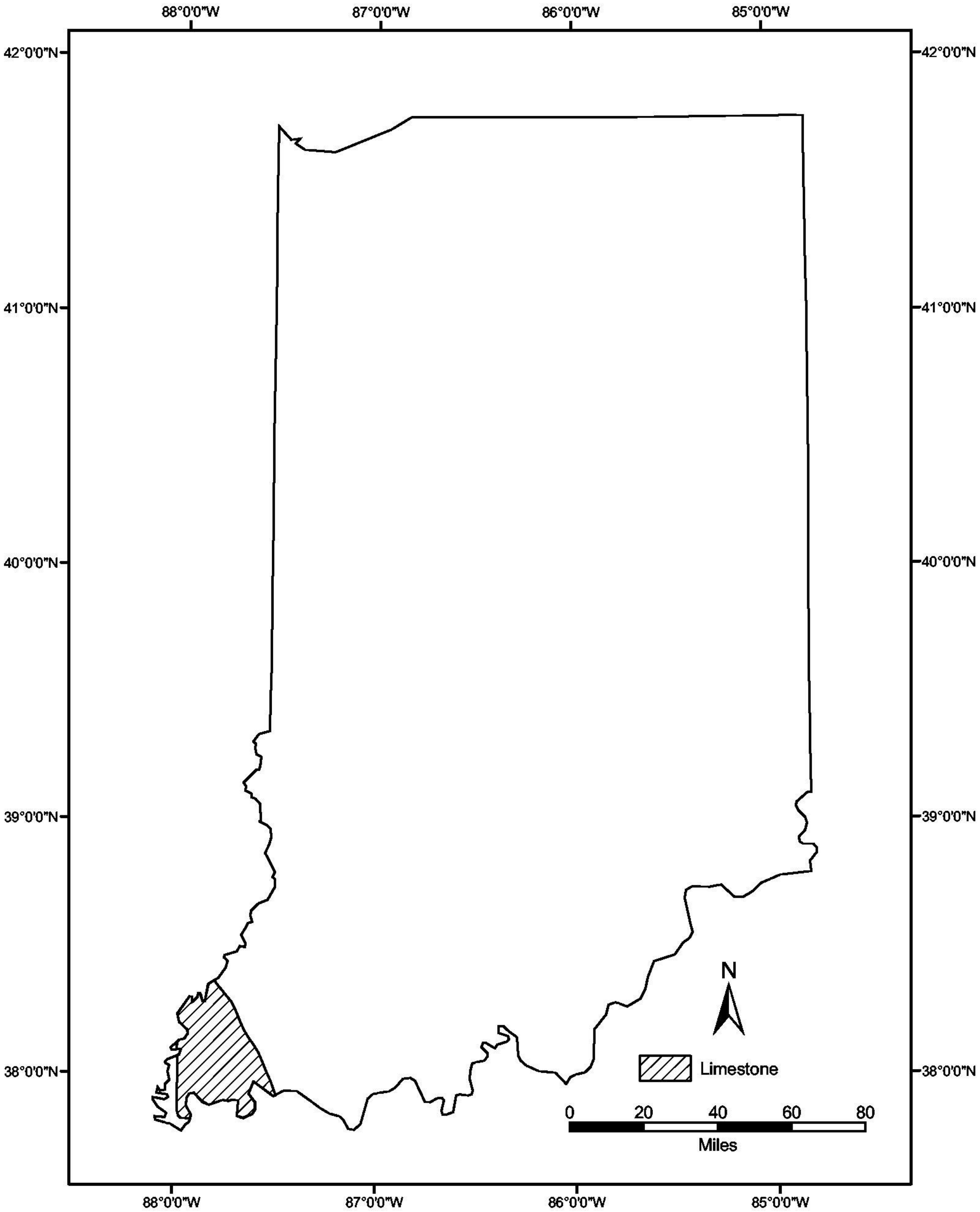

Figure M95. Limestone areas in Indiana in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Unit 6).

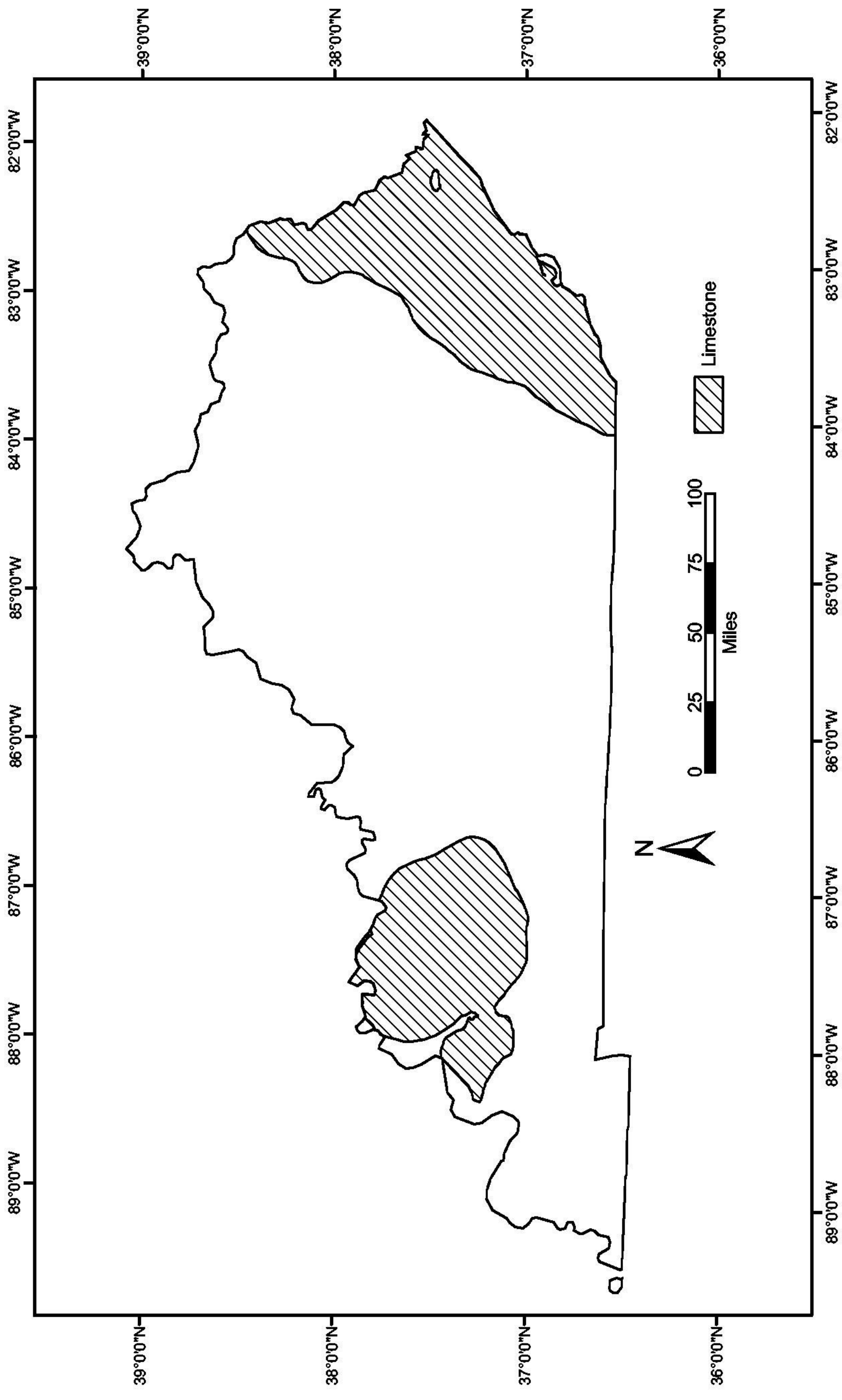

Figure M96. Limestone areas in Kentucky in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 5 and 6).

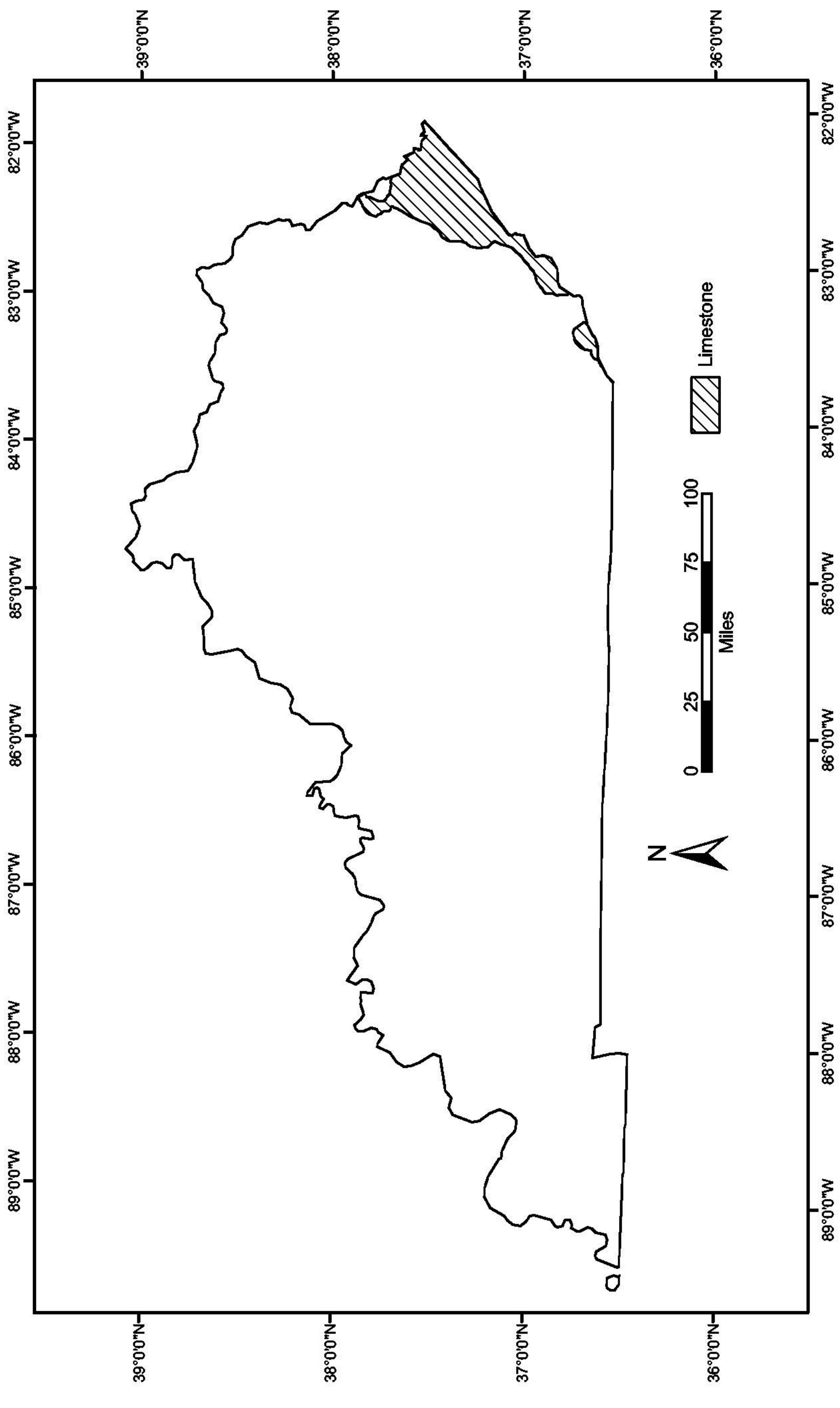

Figure M97. Limestone areas in Kentucky in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Unit 5 and 6).

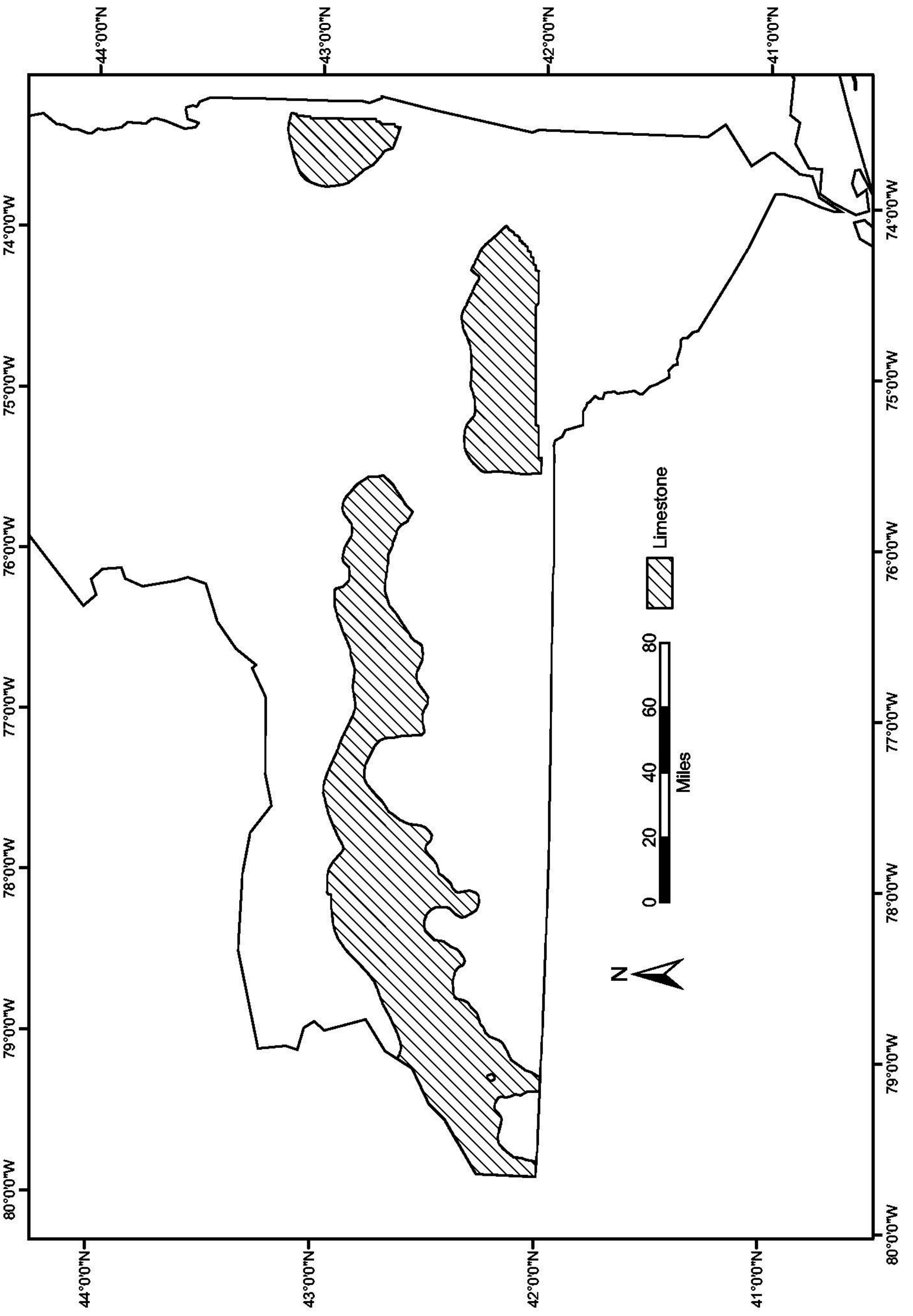

Figure M98. Limestone areas in New York in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 3, 5 and 6).

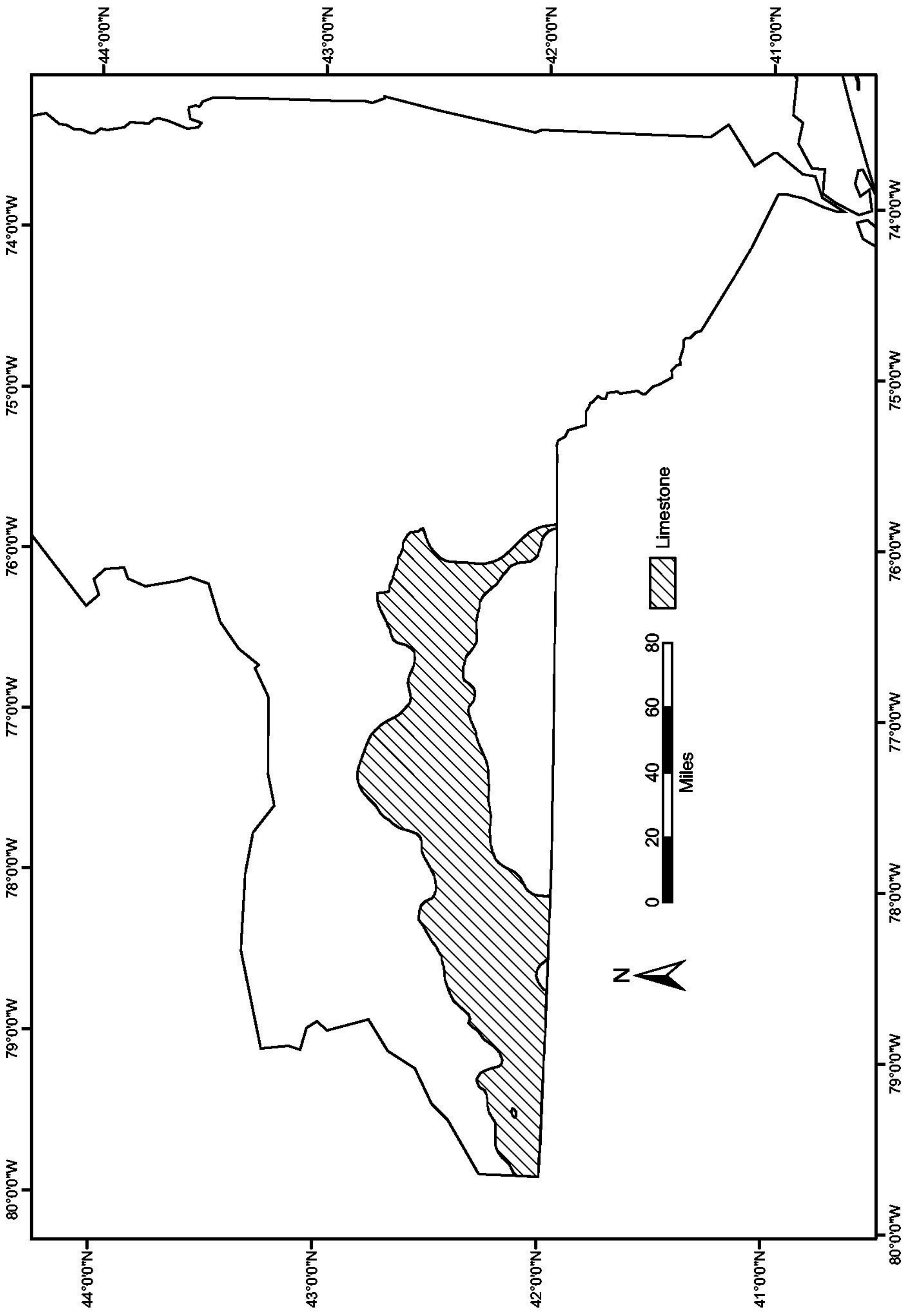

Figure M99. Limestone areas in New York in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 5 and 6).

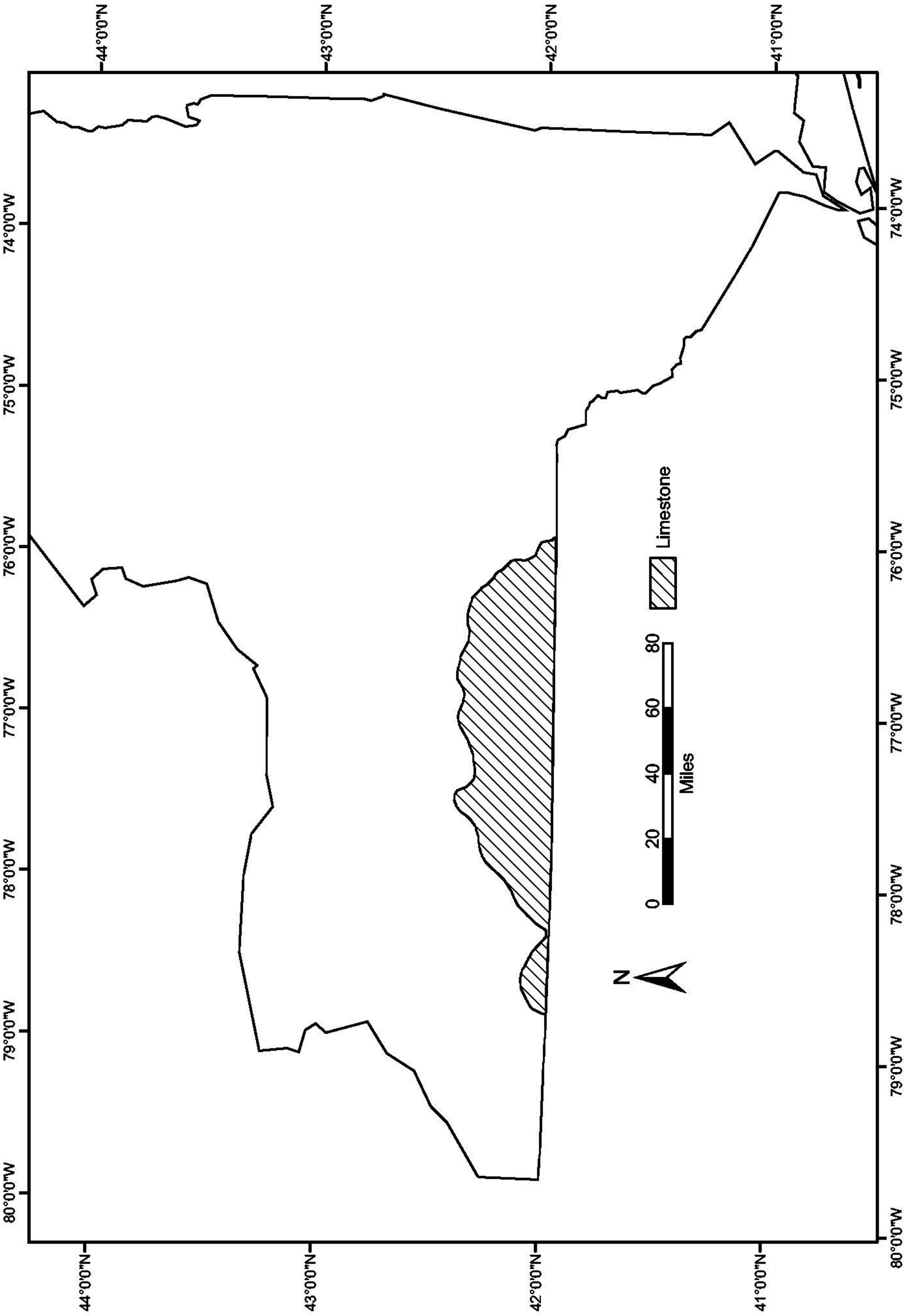

Figure M100. Limestone areas in New York in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 5 and 6).

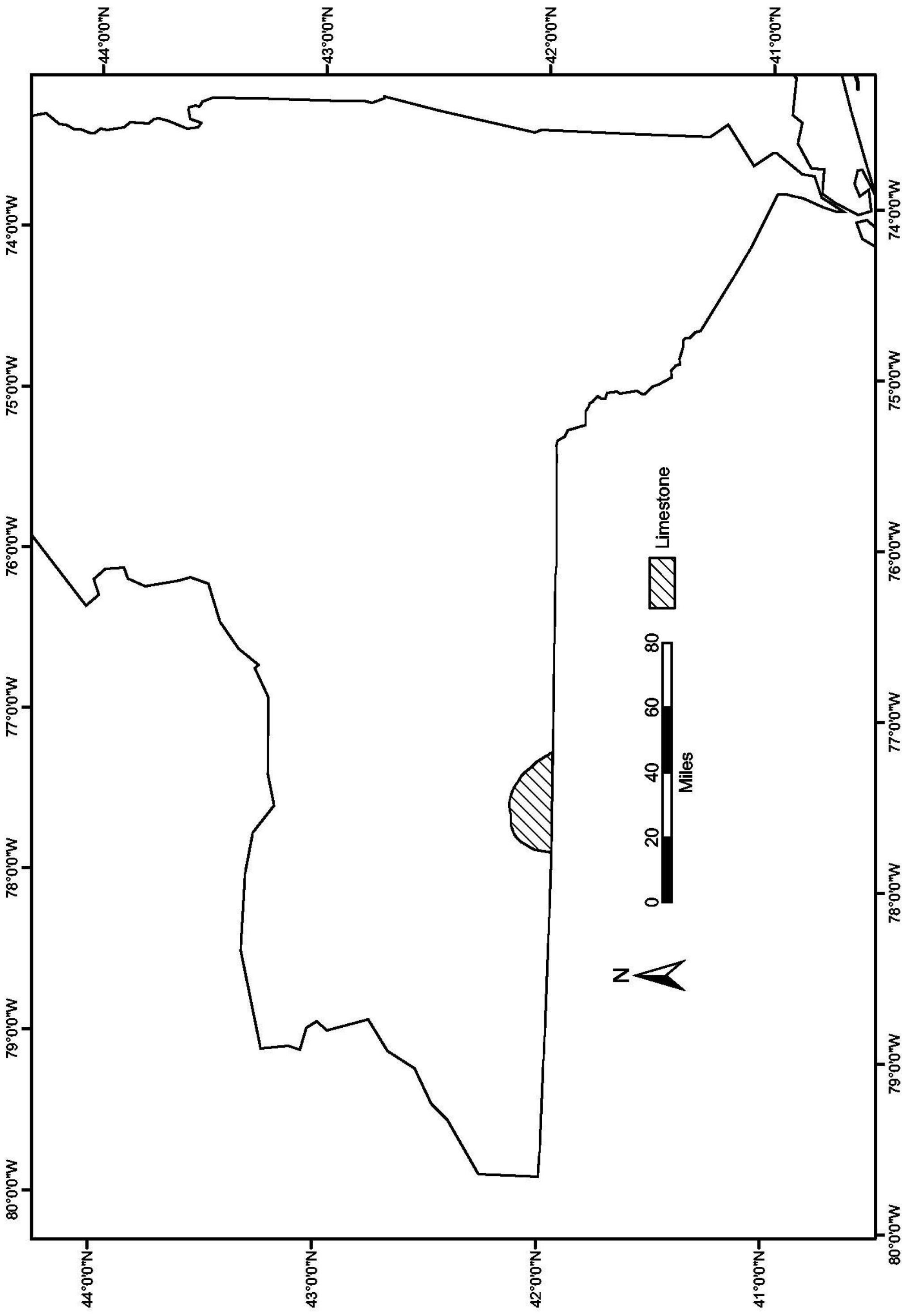

Figure M101. Limestone areas in New York in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Unit 6).

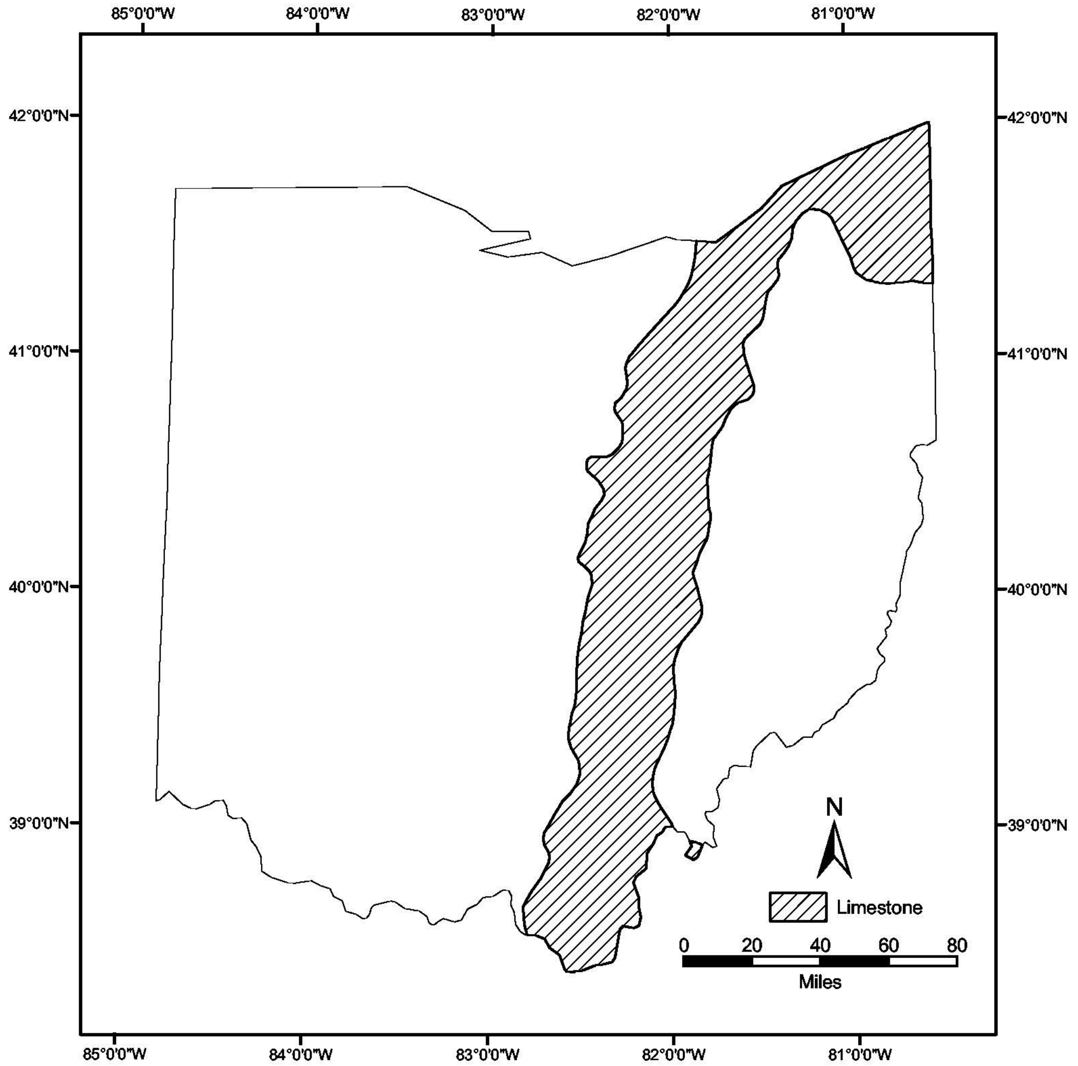

Figure M102. Limestone areas in Ohio in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Unit 6).

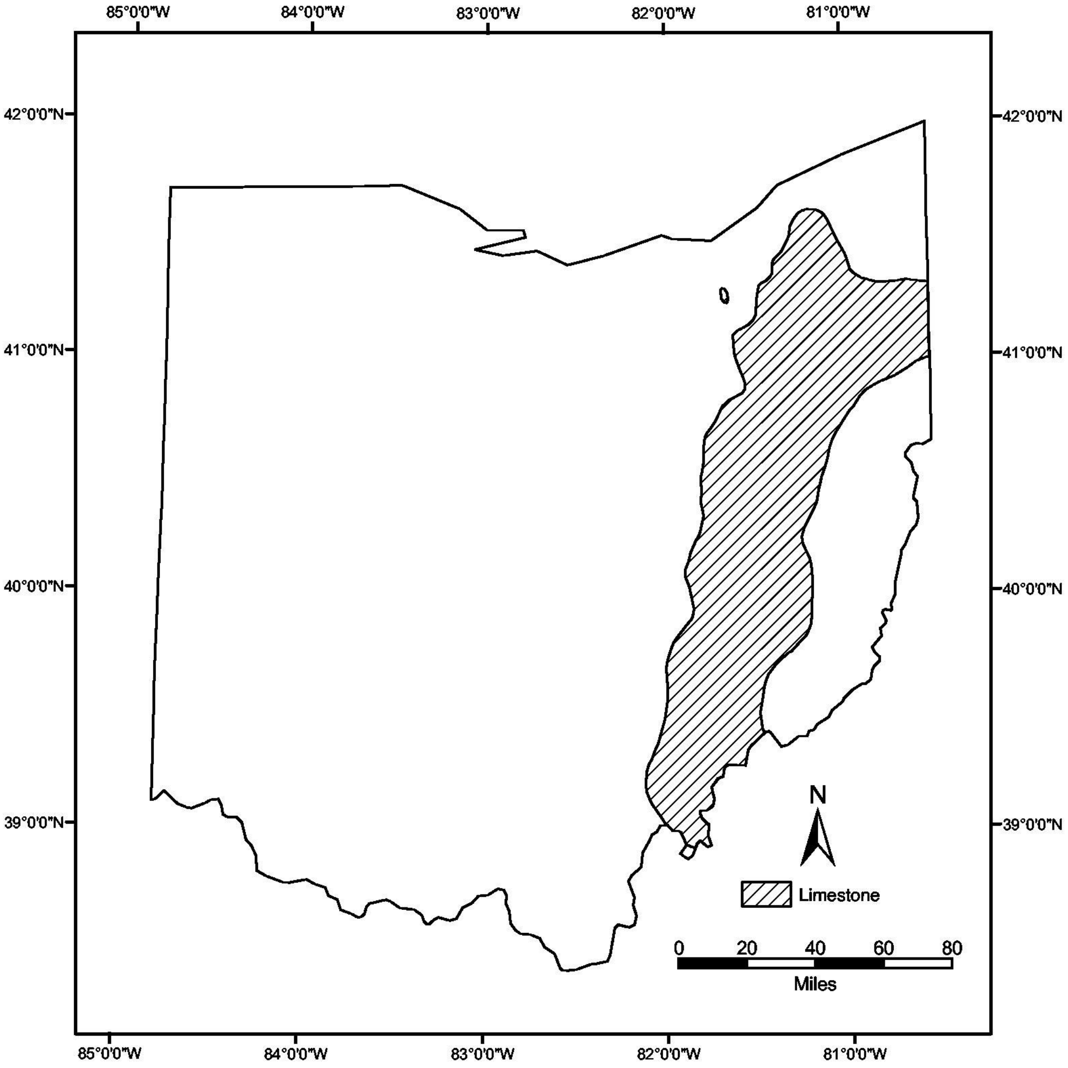

Figure M103. Limestone areas in Ohio in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Unit 6).

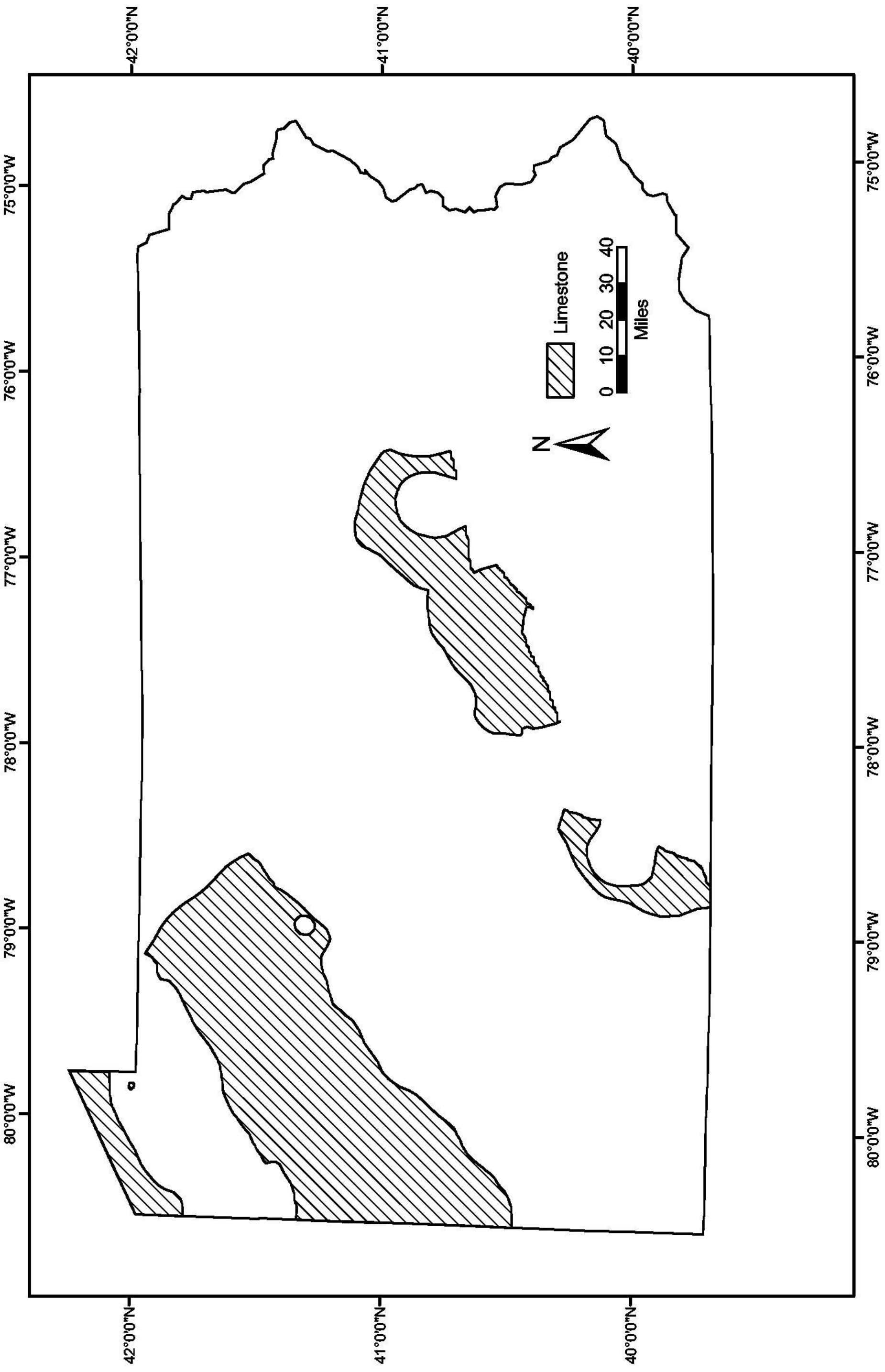

Figure M104. Limestone areas in Pennsylvania in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 3, 5, and 6).

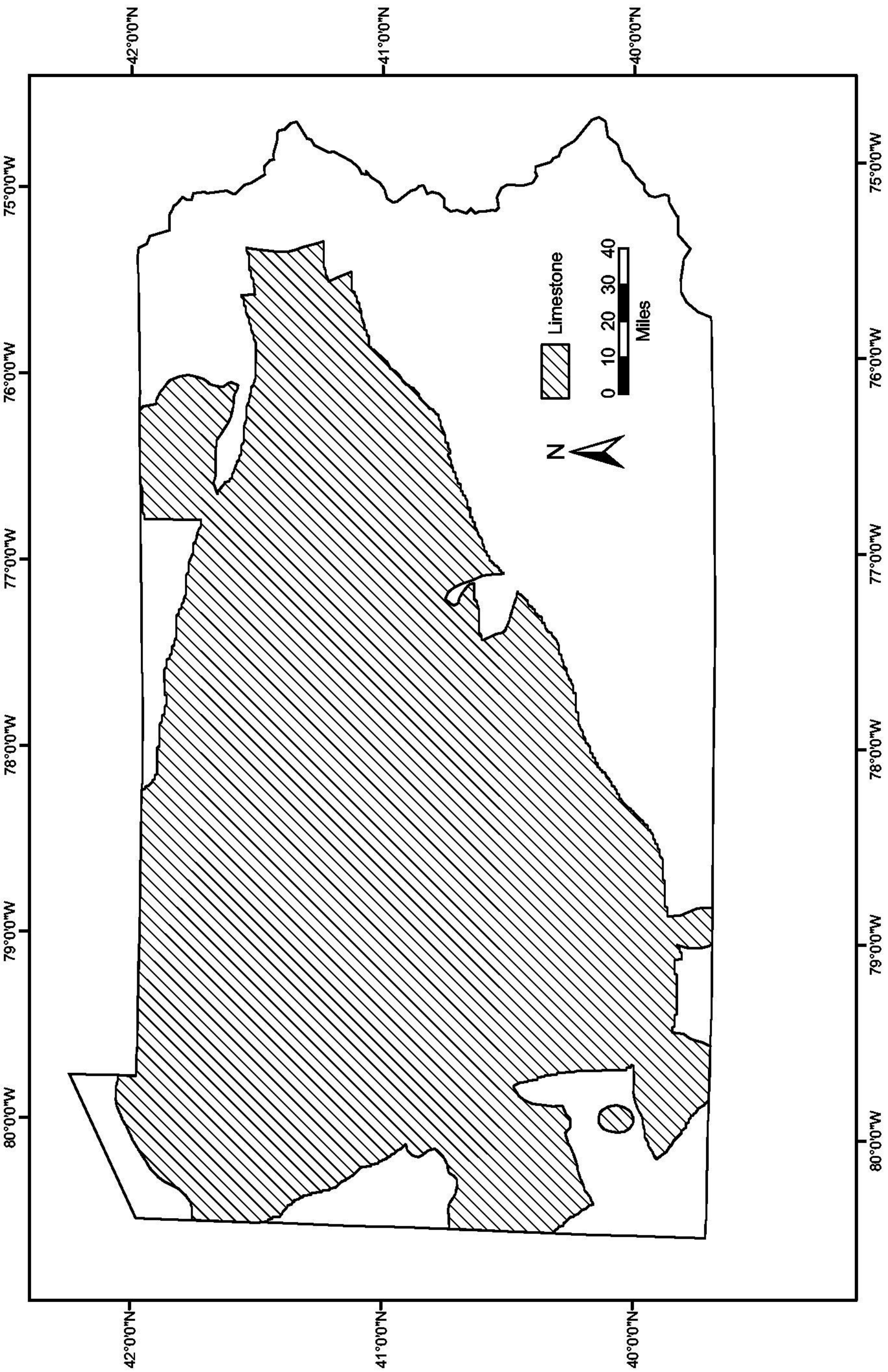

Figure M105. Limestone areas in Pennsylvania in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 2, 3, 5 and 6).

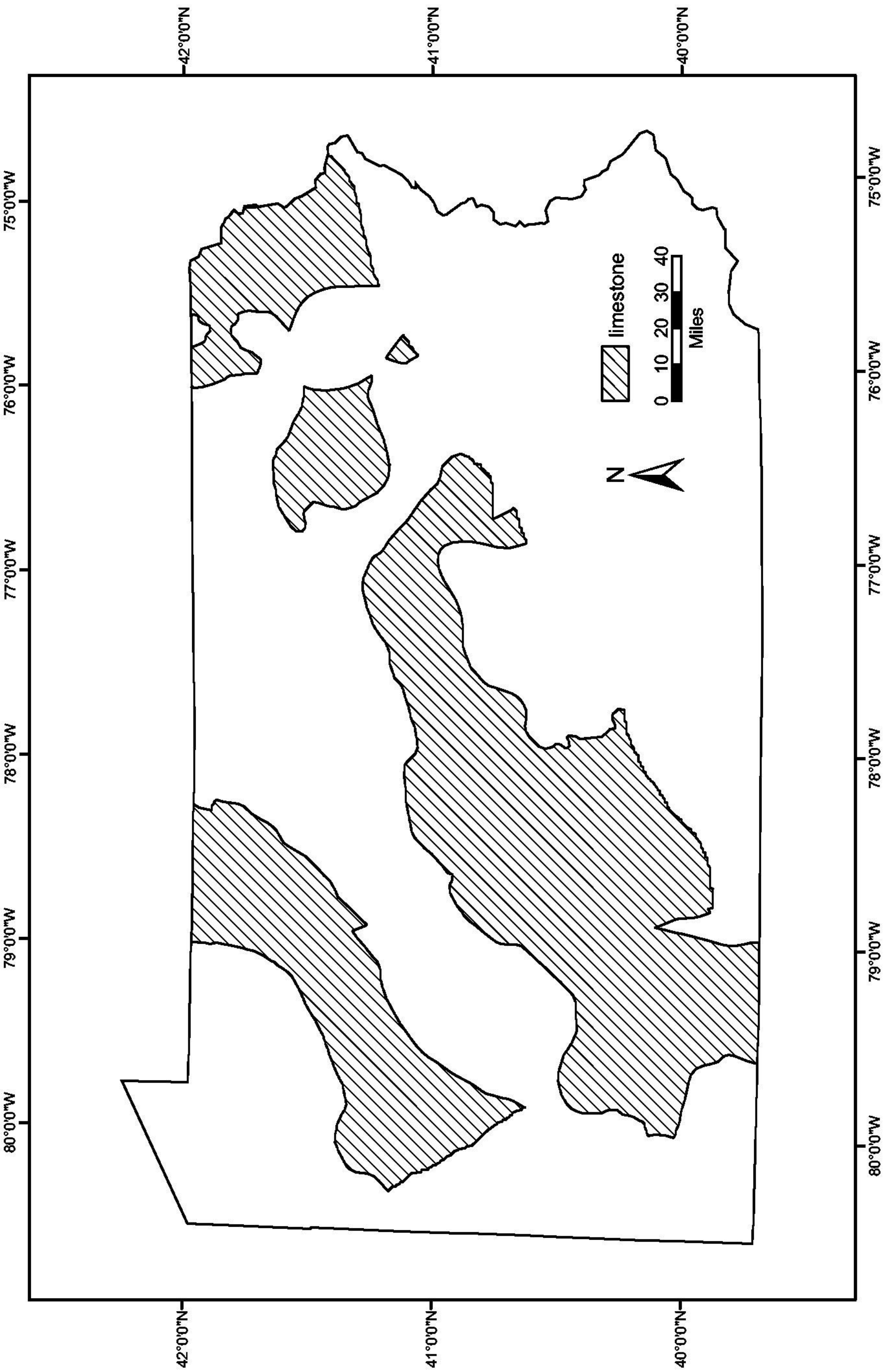

Figure M106. Limestone areas in Pennsylvania in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 3, 5 and 6).

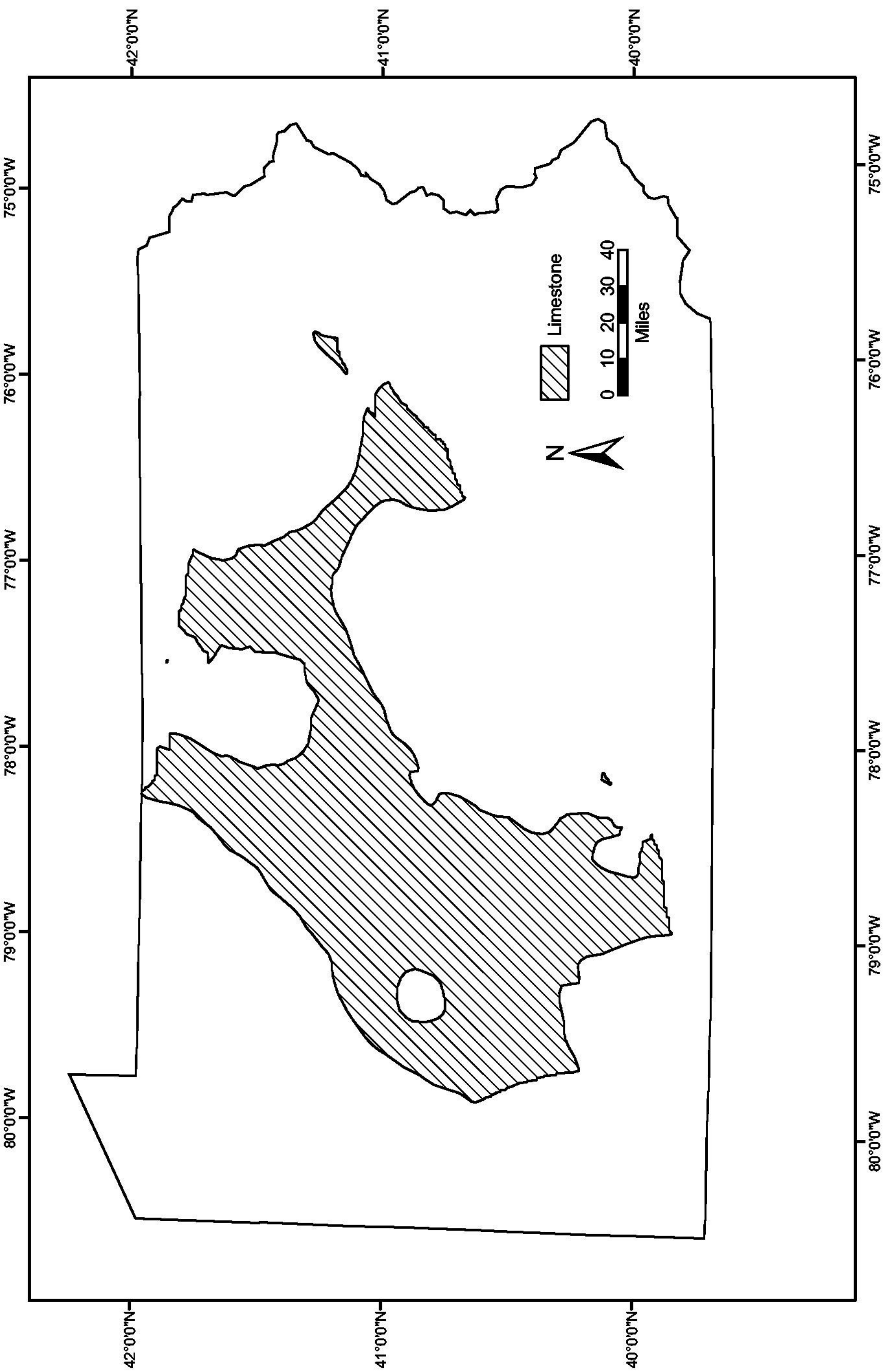

Figure M107. Limestone areas in Pennsylvania in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Units 5 and 6).

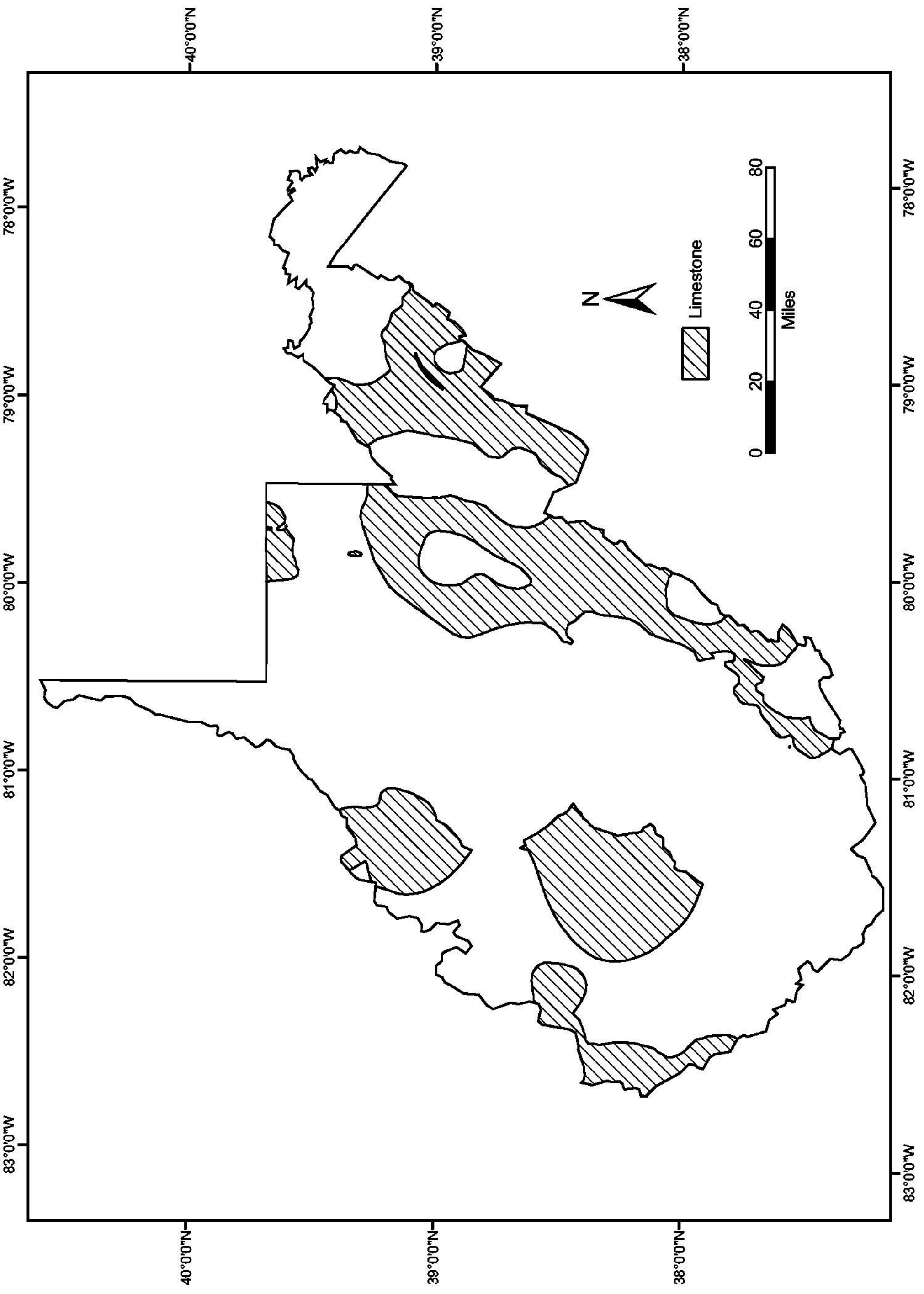

Figure M108. Limestone areas in West Virginia in the 4000 ft to 6000 ft range that are over 300 feet in thickness (Units 3, 5, and 6).

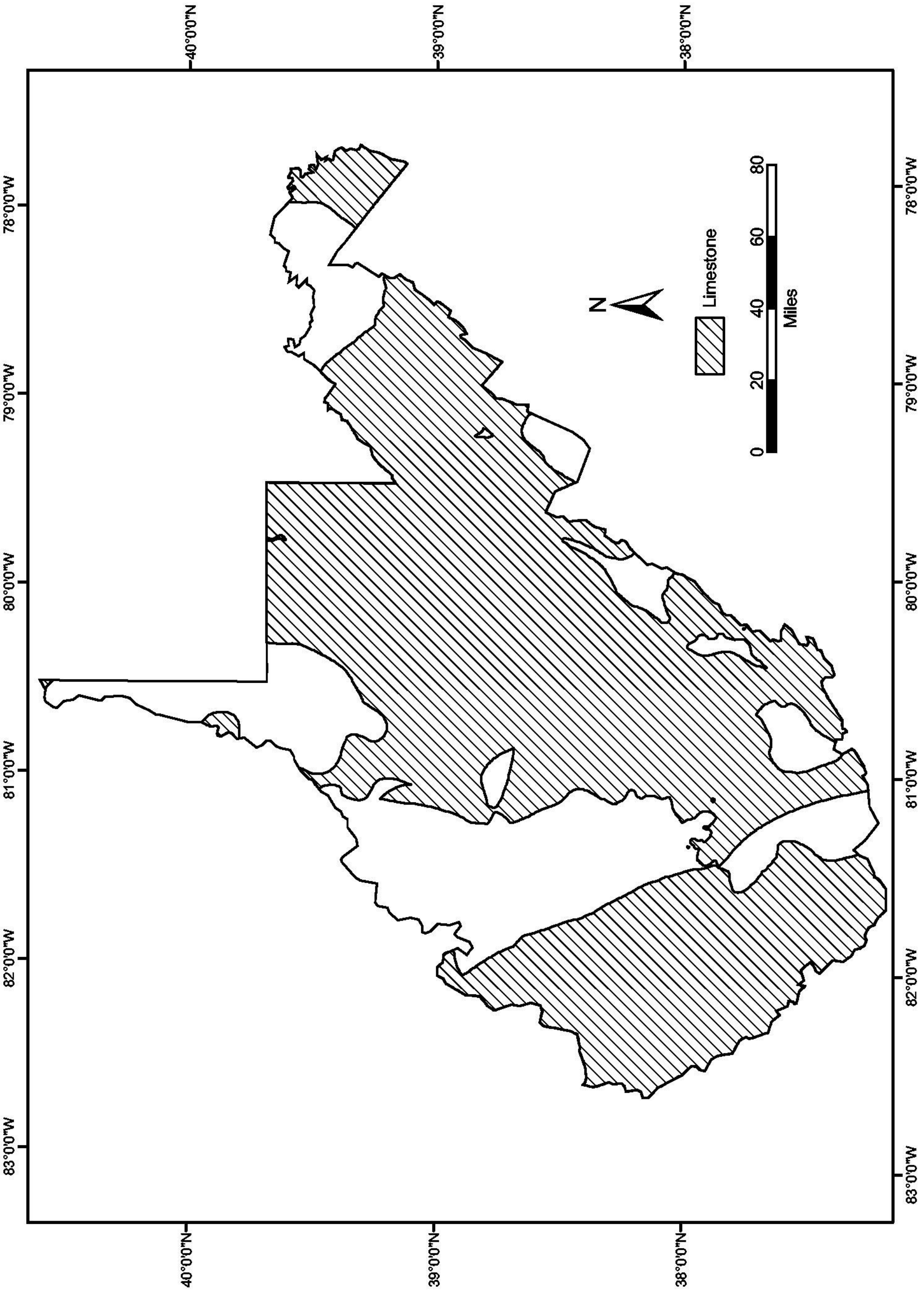

Figure M109. Limestone areas in West Virginia in the 6000 ft to 8000 ft range that are over 300 feet in thickness (Units 3, 5, and 6).

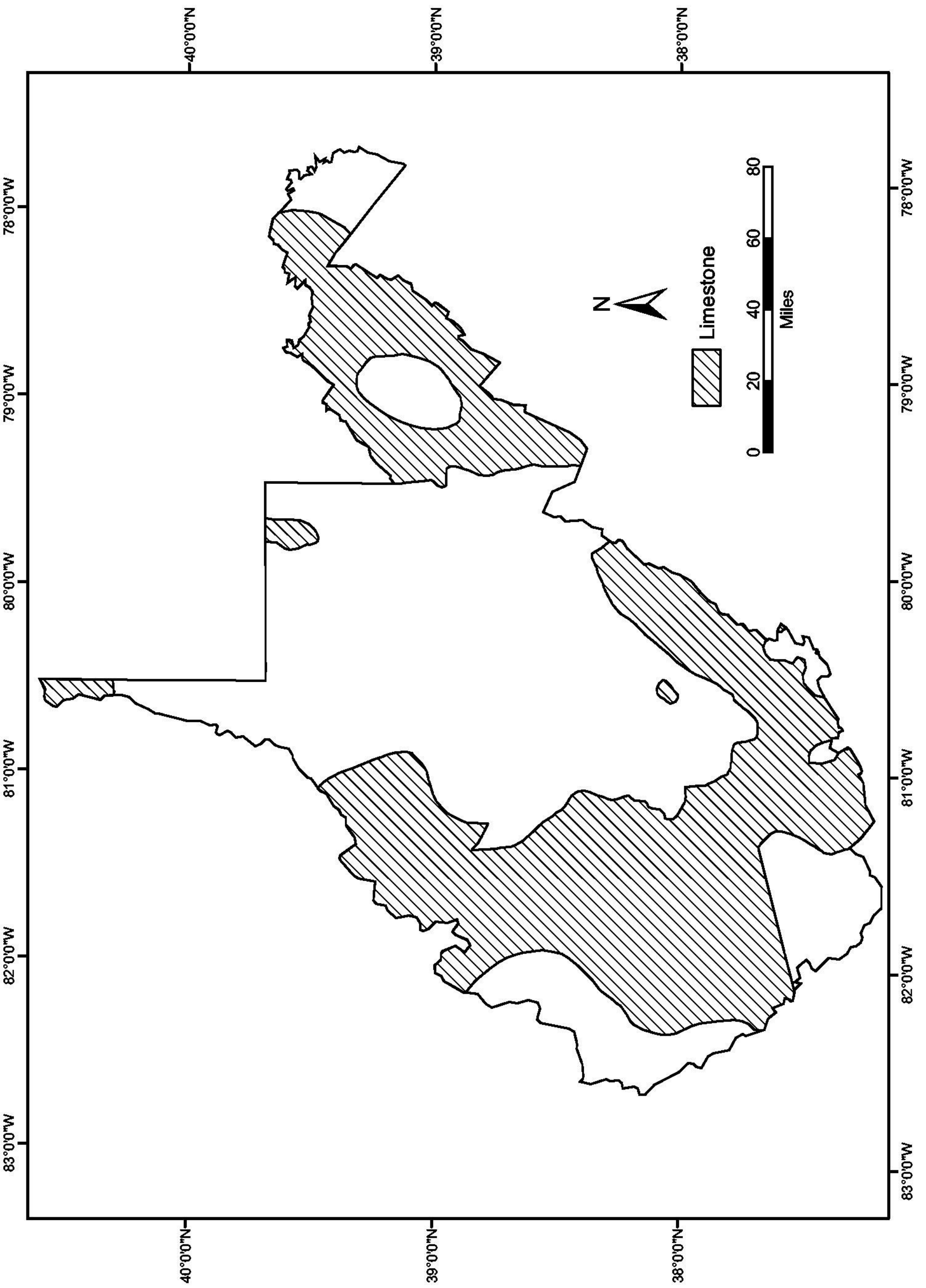

Figure M110. Limestone areas in West Virginia in the 8000 ft to 10000 ft range that are over 300 feet in thickness (Units 3, 5, and 6).

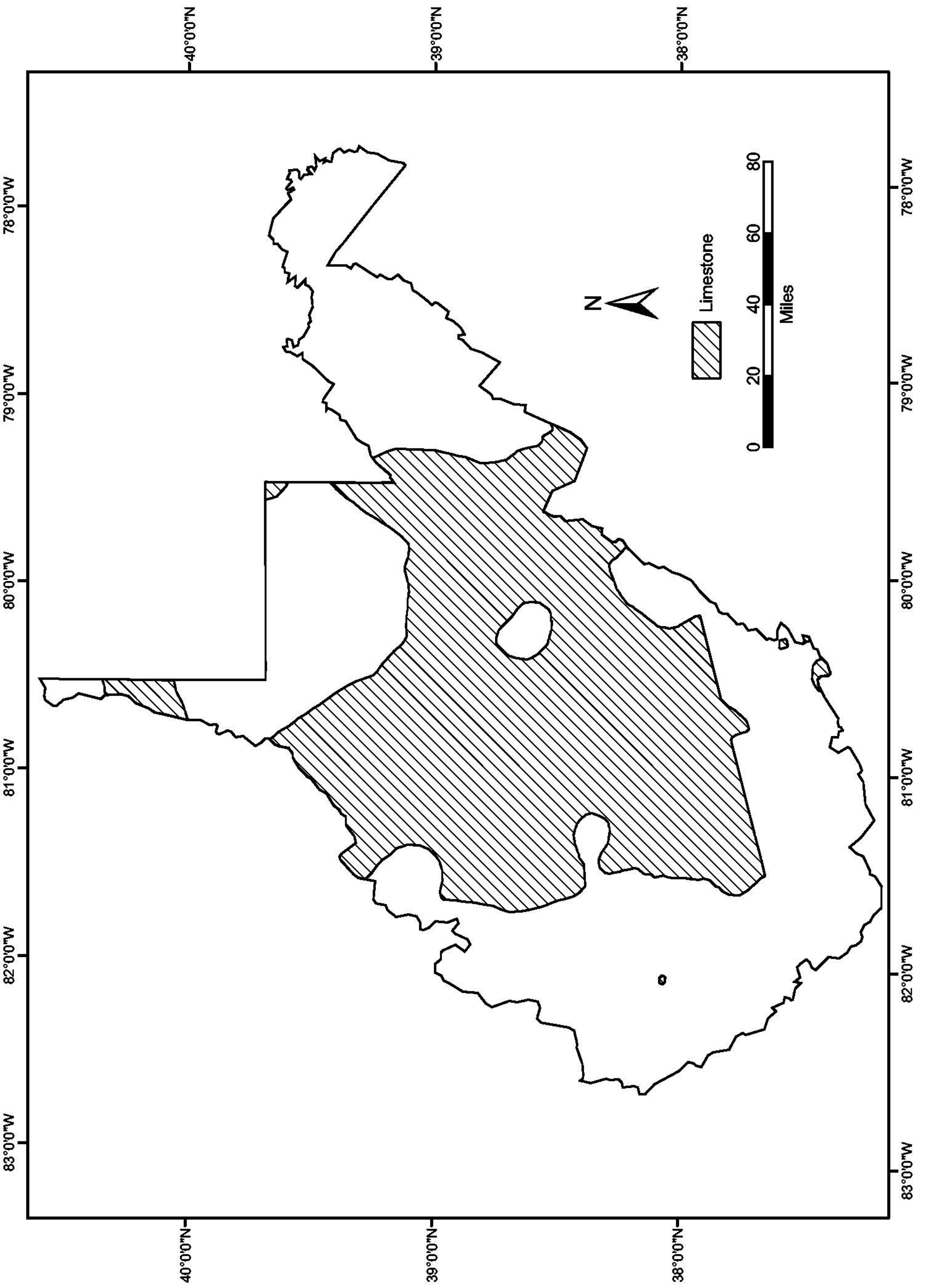

Figure M111. Limestone areas in West Virginia in the 10000 ft to 12000 ft range that are over 300 feet in thickness (Units 5 and 6).

Appendix A: Supplemental Data for Preliminary Economic Analysis

Table A1. Acid properties and costs

Acid Properties and Costs

Acid	cost $ US / ton	% Purity	Molecular Weight
hydrobromic acid (HBr)	1120	48	80.91
nitric acid (HNO3)	215	68	63.01
hydrochloric (HCl)	68	33	36.46
acetic acid (CH3COOH)	910	95	60.05
formic acid (HCOOH)	451	85	46.03
phosphoric acid (H3PO4)	2.7	52	98.00
citric acid (C6H8O7)	940	98	192.13
sulfuric acid (H2SO4)	25	100	98.07
3-hydroxypropionic acid	1000	98	90.08

Acid	Dissociated Protons	pKa
hydrobromic acid (HBr)	1	<1
nitric acid (HNO3)	1	<1
hydrochloric (HCl)	1	<1
acetic acid (CH3COOH)	1	4.756
formic acid (HCOOH)	1	3.751
phosphoric acid (H3PO4)	1	2.148, 7.198, 11.90
citric acid (C6H8O7)	2	3.128, 4.761, 6.396
sulfuric acid (H2SO4)	2	<1, 1.99
3-hydroxypropionic acid	1	4.65

	hydrobromic acid	nitric acid	hydrochloric
Acid weight % in solution =	48.00	68.00	33.00
Density of aq. Acid (g/cm3) =	1.30	1.38	1.18
Density of aq. Acid (lb/ft3) =	81.16	86.21	73.59
Mol. Weight limestone =	100.09	100.09	100.09
Mol. Weight Dry Acid =	80.91	63.01	36.46
lb aq. Acid / lb limestone=	3.37	1.85	2.21

	formic acid	phosphoric acid	citric acid
Acid weight % in solution =	85.00	52.00	98.00
Density of aq. Acid (g/cm3) =	1.22	1.41	1.67
Density of aq. Acid (lb/ft3) =	76.16	88.21	103.94
Mol. Weight limestone =	100.09	100.09	100.09
Mol. Weight Dry Acid =	46.03	98.00	192.13
lb aq. Acid / lb limestone=	1.08	3.77	1.96

	3-hydroxypropionic acid	acetic acid	sulfuric acid
Acid weight % in solution =	98.00	95.00	100.00
Density of aq. Acid (g/cm3) =		1.05	1.83
Density of aq. Acid (lb/ft3) =		65.50	114.36
Mol. Weight limestone =	100.09	100.09	100.09
Mol. Weight Dry Acid =	90.08	60.05	98.07
lb aq. Acid / lb limestone=	1.84	1.26	0.98

Table A2. Gas temperature, pressure, and density at depth.

Pressure as a function of depth

Depth (ft)	Pressure Hydrostatic (0.433 psi/ft)	Pressure Operating (0.55 psi/ft)	Pressure Fracture (0.64 psi/ft)
0	0	15	0
2000	866	1115	1280
4000	1732	2215	2560
6000	2598	3315	3840
8000	3464	4415	5120
10000	4330	5515	6400
12000	5196	6615	7680

Depth (ft)	Temperature (℃)	Gas Density@Depth (lb/ft3)	Gas Density@Depth (kg/m3)
0	11.00	0.04	0.71
2000	23.19	3.75	60.07
4000	35.38	8.00	128.15
6000	47.58	11.50	184.21
8000	59.77	13.00	208.24
10000	71.96	14.00	224.26
12000	84.15	15.00	240.28

Gas Volume@STP (BCF)	Mass of Gas (kg)	Mass of Gas (lb)
0.25	5037619.8	11105936.5
0.5	10075239.5	22211873.1
1	20150479.0	44423746.1
1.5	30225718.6	66635619.2
2	40300958.1	88847492.2

Table A3. Required storage gas volume at depth for different gas storage capacities.

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
Depth (ft)	Gas Volume@Depth (m3)	Gas Volume@Depth (m3)	Gas Volume@Depth (m3)
0	7079286	14158572	28317143
2000	83864	167727	335454
4000	39311	78622	157244
6000	27347	54694	109387
8000	24191	48383	96766
10000	22463	44927	89854
12000	20966	41932	83864

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
Depth (ft)	Gas Volume@Depth (ft3)	Gas Volume@Depth (ft3)	Gas Volume@Depth (ft3)
0	250000000	500000000	1000000000
2000	2961583	5923166	11846332
4000	1388242	2776484	5552968
6000	965734	1931467	3862934
8000	854303	1708606	3417211
10000	793281	1586562	3173125
12000	740396	1480792	2961583

Table A4. Mass of limestone needing to be removed as a function of gas storage volume, depth, and percent porosity.

Limestone Density (kg/m3)
2720.00
Limestone Density (lb/ft3)
169.80

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	0% Porosity	0% Porosity	0% Porosity
Depth (ft)	Limestone Mass (lb)	Limestone Mass (lb)	Limestone Mass (lb)
0	4.25E+10	8.49E+10	1.70E+11
2000	5.03E+08	1.01E+09	2.01E+09
4000	2.36E+08	4.71E+08	9.43E+08
6000	1.64E+08	3.28E+08	6.56E+08
8000	1.45E+08	2.90E+08	5.80E+08
10000	1.35E+08	2.69E+08	5.39E+08
12000	1.26E+08	2.51E+08	5.03E+08

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	5% Porosity	5% Porosity	5% Porosity
Depth (ft)	Limestone Mass (lb)	Limestone Mass (lb)	Limestone Mass (lb)
0	4.03E+10	8.07E+10	1.61E+11
2000	4.78E+08	9.55E+08	1.91E+09
4000	2.24E+08	4.48E+08	8.96E+08
6000	1.56E+08	3.12E+08	6.23E+08
8000	1.38E+08	2.76E+08	5.51E+08
10000	1.28E+08	2.56E+08	5.12E+08
12000	1.19E+08	2.39E+08	4.78E+08

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	10% Porosity	10% Porosity	10% Porosity
Depth (ft)	Limestone Mass (lb)	Limestone Mass (lb)	Limestone Mass (lb)
0	3.82E+10	7.64E+10	1.53E+11
2000	4.53E+08	9.05E+08	1.81E+09
4000	2.12E+08	4.24E+08	8.49E+08
6000	1.48E+08	2.95E+08	5.90E+08
8000	1.31E+08	2.61E+08	5.22E+08
10000	1.21E+08	2.42E+08	4.85E+08
12000	1.13E+08	2.26E+08	4.53E+08

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	15% Porosity	15% Porosity	15% Porosity
Depth (ft)	Limestone Mass (lb)	Limestone Mass (lb)	Limestone Mass (lb)
0	3.61E+10	7.22E+10	1.44E+11
2000	4.27E+08	8.55E+08	1.71E+09
4000	2.00E+08	4.01E+08	8.01E+08
6000	1.39E+08	2.79E+08	5.58E+08
8000	1.23E+08	2.47E+08	4.93E+08
10000	1.14E+08	2.29E+08	4.58E+08
12000	1.07E+08	2.14E+08	4.27E+08

Table A5. Hydrochloric acid properties.

HCL weight % in solution = 33.000
Density of aq. HCL (g/cm3) = 1.170
Density of aq. HCL (lb/ft3) = 73.041
Mol. Weight limestone = 100.089
Mol. Weight dry HCl = 36.461
Gallons of HCL/Metric ton = 225.784
lb aq. HCl / lb limestone= 2.208

Table A6. Quantity of aqueous hydrochloric acid needed to remove limestone as a function of gas storage volume, depth, and percent porosity.

Depth (ft)	0.25 BCF of Gas 0% Porosity Weight Aq. HCl (metric ton)	0.5 BCF of Gas 0% Porosity Weight Aq. HCl (metric ton)	1.0 BCF of Gas 0% Porosity Weight Aq. HCl (metric ton)
0	4.25E+07	8.50E+07	1.70E+08
2000	5.04E+05	1.01E+06	2.01E+06
4000	2.36E+05	4.72E+05	9.44E+05
6000	1.64E+05	3.28E+05	6.57E+05
8000	1.45E+05	2.91E+05	5.81E+05
10000	1.35E+05	2.70E+05	5.40E+05
12000	1.26E+05	2.52E+05	5.04E+05

Depth (ft)	0.25 BCF of Gas 5% Porosity Weight Aq. HCl (metric ton)	0.5 BCF of Gas 5% Porosity Weight Aq. HCl (metric ton)	1.0 BCF of Gas 5% Porosity Weight Aq. HCl (metric ton)
0	4.04E+07	8.08E+07	1.62E+08
2000	4.78E+05	9.57E+05	1.91E+06
4000	2.24E+05	4.49E+05	8.97E+05
6000	1.56E+05	3.12E+05	6.24E+05
8000	1.38E+05	2.76E+05	5.52E+05
10000	1.28E+05	2.56E+05	5.13E+05
12000	1.20E+05	2.39E+05	4.78E+05

Depth (ft)	0.25 BCF of Gas 10% Porosity Weight Aq. HCl (metric ton)	0.5 BCF of Gas 10% Porosity Weight Aq. HCl (metric ton)	1.0 BCF of Gas 10% Porosity Weight Aq. HCl (metric ton)
0	3.83E+07	7.65E+07	1.53E+08
2000	4.53E+05	9.07E+05	1.81E+06
4000	2.12E+05	4.25E+05	8.50E+05
6000	1.48E+05	2.96E+05	5.91E+05
8000	1.31E+05	2.61E+05	5.23E+05
10000	1.21E+05	2.43E+05	4.86E+05
12000	1.13E+05	2.27E+05	4.53E+05

Depth (ft)	0.25 BCF of Gas 15% Porosity Weight Aq. HCl (metric ton)	0.5 BCF of Gas 15% Porosity Weight Aq. HCl (metric ton)	1.0 BCF of Gas 15% Porosity Weight Aq. HCl (metric ton)
0	3.61E+07	7.23E+07	1.45E+08
2000	4.28E+05	8.56E+05	1.71E+06
4000	2.01E+05	4.01E+05	8.03E+05
6000	1.40E+05	2.79E+05	5.58E+05
8000	1.23E+05	2.47E+05	4.94E+05
10000	1.15E+05	2.29E+05	4.59E+05
12000	1.07E+05	2.14E+05	4.28E+05

Table A7. Aqueous hydrochloric acid cost as a function of gas storage volume, depth, and percent porosity.

Depth (ft)	0.25 BCF of Gas 0% Porosity Cost ($ US millions)	0.5 BCF of Gas 0% Porosity Cost ($ US millions)	1.0 BCF of Gas 0% Porosity Cost ($ US millions)
0	3188.45	6376.90	12753.80
2000	37.77	75.54	151.09
4000	17.71	35.41	70.82
6000	12.32	24.63	49.27
8000	10.90	21.79	43.58
10000	10.12	20.23	40.47
12000	9.44	18.89	37.77

Depth (ft)	0.25 BCF of Gas 5% Porosity Cost ($ US millions)	0.5 BCF of Gas 5% Porosity Cost ($ US millions)	1.0 BCF of Gas 5% Porosity Cost ($ US millions)
0	3029.03	6058.05	12116.11
2000	35.88	71.77	143.53
4000	16.82	33.64	67.28
6000	11.70	23.40	46.80
8000	10.35	20.70	41.40
10000	9.61	19.22	38.45
12000	8.97	17.94	35.88

Depth (ft)	0.25 BCF of Gas 10% Porosity Cost ($ US millions)	0.5 BCF of Gas 10% Porosity Cost ($ US millions)	1.0 BCF of Gas 10% Porosity Cost ($ US millions)
0	2869.60	5739.21	11478.42
2000	33.99	67.99	135.98
4000	15.93	31.87	63.74
6000	11.09	22.17	44.34
8000	9.81	19.61	39.22
10000	9.11	18.21	36.42
12000	8.50	17.00	33.99

Depth (ft)	0.25 BCF of Gas 15% Porosity Cost ($ US millions)	0.5 BCF of Gas 15% Porosity Cost ($ US millions)	1.0 BCF of Gas 15% Porosity Cost ($ US millions)
0	2710.18	5420.36	10840.73
2000	32.11	64.21	128.42
4000	15.05	30.10	60.20
6000	10.47	20.94	41.88
8000	9.26	18.52	37.05
10000	8.60	17.20	34.40
12000	8.03	16.05	32.11

Table A8. Purchased equipment costs.

Costs/Purchased equipment Costs

	Cost ($ US)	
Process Control Facility	85000	
Pumps	50000	Sealless centrifugal pump, acid resistant
Acid Storage Tanks	250000	
Valves and Piping	198000	
Sedementation Pond	50000	
Multieffect Evaporator	110000	
Wetlands Treatment Area	30000	
Land	210000	Assume 15 acres needed at a cost of $14,000/acre
Total Capital Cost	**983000**	
Equipment Costs		
Pumps	85000	
Acid Storage Tanks	265000	
Clarifier (10 ft diam.)	449640	
Wetlands	30000	
Purchased Equipment Cost	799640	

	Lang Factors	Cost ($ US)
Purchased equipment	100	799640
Installation	39	311860
Instrumentation	13	103953
Piping	31	247888
Electrical	10	79964
Buildings	29	231896
Yard Improvements	10	79964
Service facilities	55	439802
Land	2	15993
Engineering & Supervision	32	255885
Construction expenses	34	271878
Contractor's fee	18	143935
Contingency	36	287871
Total Erected Cost	409	3270529

Table A9. Calcium chloride pricing information.

Product Form	Weight Percent CaCl2	Sale Price ($ US/ton)	Price/ton dry CaCl2 ($US)
80% flake	80	200	2.50E+02
95% flake	95	275	2.89E+02
35% aq. solution	35	132	3.77E+02
45% aq. solution	45	160	3.56E+02

Chemical Market Reporter - Dec. 16th, ton = 2000 lb

Assume that some fraction of the CaCl2 product from the cavern can be converted into saleable product.

Fraction Saleable = 0.75

	Molecular Weight
CaCl2	110.986
CaCO3	100.089

Table A10. Value of calcium chloride products as a function of gas storage volume, depth, and percent porosity.

Assume the **product will be sold as a 80% flake**!

Depth (ft)	0.25 BCF of Gas 0% Porosity CaCl2 Value ($ US millions)	0.5 BCF of Gas 0% Porosity CaCl2 Value ($ US millions)	1.0 BCF of Gas 0% Porosity CaCl2 Value ($ US millions)
0	4413.07	8826.15	17652.30
2000	52.28	104.56	209.11
4000	24.51	49.01	98.02
6000	17.05	34.09	68.19
8000	15.08	30.16	60.32
10000	14.00	28.01	56.01
12000	13.07	26.14	52.28

Depth (ft)	0.25 BCF of Gas 5% Porosity CaCl2 Value ($ US millions)	0.5 BCF of Gas 5% Porosity CaCl2 Value ($ US millions)	1.0 BCF of Gas 5% Porosity CaCl2 Value ($ US millions)
0	4192.42	8384.84	16769.68
2000	49.66	99.33	198.66
4000	23.28	46.56	93.12
6000	16.20	32.39	64.78
8000	14.33	28.65	57.31
10000	13.30	26.61	53.21
12000	12.42	24.83	49.66

Depth (ft)	0.25 BCF of Gas 10% Porosity CaCl2 Value ($ US millions)	0.5 BCF of Gas 10% Porosity CaCl2 Value ($ US millions)	1.0 BCF of Gas 10% Porosity CaCl2 Value ($ US millions)
0	3971.77	7943.53	15887.07
2000	47.05	94.10	188.20
4000	22.06	44.11	88.22
6000	15.34	30.69	61.37
8000	13.57	27.14	54.29
10000	12.60	25.21	50.41
12000	11.76	23.53	47.05

Depth (ft)	0.25 BCF of Gas 15% Porosity CaCl2 Value ($ US millions)	0.5 BCF of Gas 15% Porosity CaCl2 Value ($ US millions)	1.0 BCF of Gas 15% Porosity CaCl2 Value ($ US millions)
0	3751.11	7502.23	15004.45
2000	44.44	88.87	177.75
4000	20.83	41.66	83.32
6000	14.49	28.98	57.96
8000	12.82	25.64	51.27
10000	11.90	23.81	47.61
12000	11.11	22.22	44.44

Table A11. Total Gross Earnings Cost as a function of gas storage volume, depth, and percent porosity.

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	0% Porosity	0% Porosity	0% Porosity
Depth (ft)	Total Cost ($ US millions)	Total Cost ($ US millions)	Total Cost ($ US millions)
0			
2000			
4000	12.06	23.69	46.94
6000	8.97	17.06	33.23
8000	8.73	15.89	30.20
10000	9.16	15.80	29.09
12000	9.90	16.10	28.51

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	5% Porosity	5% Porosity	5% Porosity
Depth (ft)	Total Cost ($ US millions)	Total Cost ($ US millions)	Total Cost ($ US millions)
0			
2000			
4000	11.48	22.52	44.62
6000	8.56	16.25	31.62
8000	8.37	15.17	28.77
10000	8.82	15.14	27.76
12000	9.59	15.48	27.27

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	10% Porosity	10% Porosity	10% Porosity
Depth (ft)	Total Cost ($ US millions)	Total Cost ($ US millions)	Total Cost ($ US millions)
0			
2000			
4000	10.89	21.36	42.29
6000	8.16	15.44	30.00
8000	8.01	14.45	27.33
10000	8.49	14.47	26.43
12000	9.28	14.86	26.03

	0.25 BCF of Gas	0.5 BCF of Gas	1.0 BCF of Gas
	15% Porosity	15% Porosity	15% Porosity
Depth (ft)	Total Cost ($ US millions)	Total Cost ($ US millions)	Total Cost ($ US millions)
0			
2000			
4000	10.31	20.20	39.96
6000	7.75	14.63	28.38
8000	7.66	13.74	25.90
10000	8.16	13.81	25.10
12000	8.97	14.24	24.78