

**PS Explorations in TOC for Assessment of CO<sub>2</sub> Storage and Enhanced Gas Recovery  
for the Middle Devonian Marcellus and Upper Ordovician Utica Shales  
for the Midwest Regional Carbon Sequestration Partnership\***

**Brandon C. Nuttall<sup>1</sup>, Thomas N. Sparks<sup>1</sup>, and Stephen F. Greb<sup>1</sup>**

Search and Discovery Article #80689 (2019)\*\*

Posted July 22, 2019

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**Abstract**

The potential for carbon storage and enhanced gas recovery in the Middle Devonian Marcellus and Upper Ordovician Utica organic-rich shales in the Appalachian Basin is being investigated using methods developed during investigation of the Upper Devonian Ohio Shale. Laboratory analysis of core and well cuttings provides baseline data for modeling TOC content in shale. In general, continuous resource plays exhibit relationships between measured TOC and wireline log data. TOC is in turn related to gas content and storage capacity. Wireline-based petrophysical models for estimating TOC have been proposed by many authors, but choice and application of a model depends on data availability. Only those based on total gamma-ray and bulk-density log data were used in this study, because they are most regionally available.

For the Marcellus, multiple models were analyzed to estimate TOC from log data. The simplest model for estimating TOC is a linear regression of a density and TOC cross plot based on laboratory data because TOC is generally regarded as the main control on density changes in an organic-rich shale. Gamma-ray- and density-based models use the slope of the gamma ray-density cross plot. A median TOC curve (P50) was calculated using multiple models to provide a probabilistic summary of TOC by well, which was used as input to geospatial modeling.

The Utica Shale was deposited in a carbonate-dominated open-marine shelf setting, suggesting that organic matter types and their mode of preservation differ significantly from those of the Marcellus. Classic models to estimate TOC for organic-rich shale may not provide acceptable results. Laboratory TOC and digital well-log data were compiled by the Utica Shale Consortium. Leco TOC data were depth-matched with gamma-ray and bulk-density data from logs. Neutron-porosity and photoelectric effect data were collected, but limited digital data precluded their use. Gamma-ray and density data were used to assess existing TOC models and formulate new ones. Two new models for calculating TOC from well-log data are proposed based on best-fit correlations to the distribution of laboratory TOC data.

## Selected References

De Witt Jr., W., J.B. Roen, and L.G. Wallace, 1993, Stratigraphy of Devonian black shales and associated rocks in the Appalachian Basin, *in* J.B. Roen, and R.C. Kepferle, eds., Petroleum geology of the Devonian and Mississippian black shale of eastern North America: USGS Bulletin 1909, p. B1-B57.

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Milici, R.C., 1996, Play Dbg: Upper Devonian fractured black shales and siltstones, *in* J.B. Roen, and B.J. Walker, 1996, The Atlas of Major Appalachian Gas Plays: West Virginia Geological and Economic Survey Publication V-25, p. 86-92.

Nuttall, B.C., J.A. Drahovzal, C.F. Eble, and R.M. Bustin, 2009, Regional assessment of suitability of organic-rich gas shales for carbon sequestration: An example from the Devonian shales of the Illinois and Appalachian basins, Kentucky, *in* M. Grobe, J.C. Pashin, and R.L. Dodge, eds., Carbon dioxide sequestration in geological media - State of the science: AAPG Studies in Geology 59, p. 173-190.

Patchen, D.G., K.L. Avary, and R.B. Erwin, 1985, Correlation of Stratigraphic Units of North America (COSUNA) project - Northern Appalachian Region, and Southern Appalachian Region: AAPG, 2 sheets.

Patchen, D.G., and K.M. Carter, eds., 2015, A geologic play book for Utica Shale Appalachian Basin exploration, final report of the Utica Shale Appalachian basin exploration consortium, p. 22-35. Website accessed July 9, 2019.  
<http://www.wvgs.wvnet.edu/utica>.

Schmoker, J.W., 1993, Use of formation-density logs to determine organic-carbon content in Devonian shales of the western Appalachian basin and an additional example based on the Bakken Formation of the Williston basin, *in* J.B. Roen, and R.C. Kepferle, eds., Petroleum geology of the Devonian and Mississippian black shale of eastern North America: U.S. Geological Survey Bulletin 1909, p. J1-J14.

Wang, G., A. Shahkarami, and J. Bruno, 2016, TOC Prediction Analysis of Utica-Point Pleasant Formations in the Appalachian Basin: [AAPG Search and Discovery Article #51283 \(2016\)](#).



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Marcellus

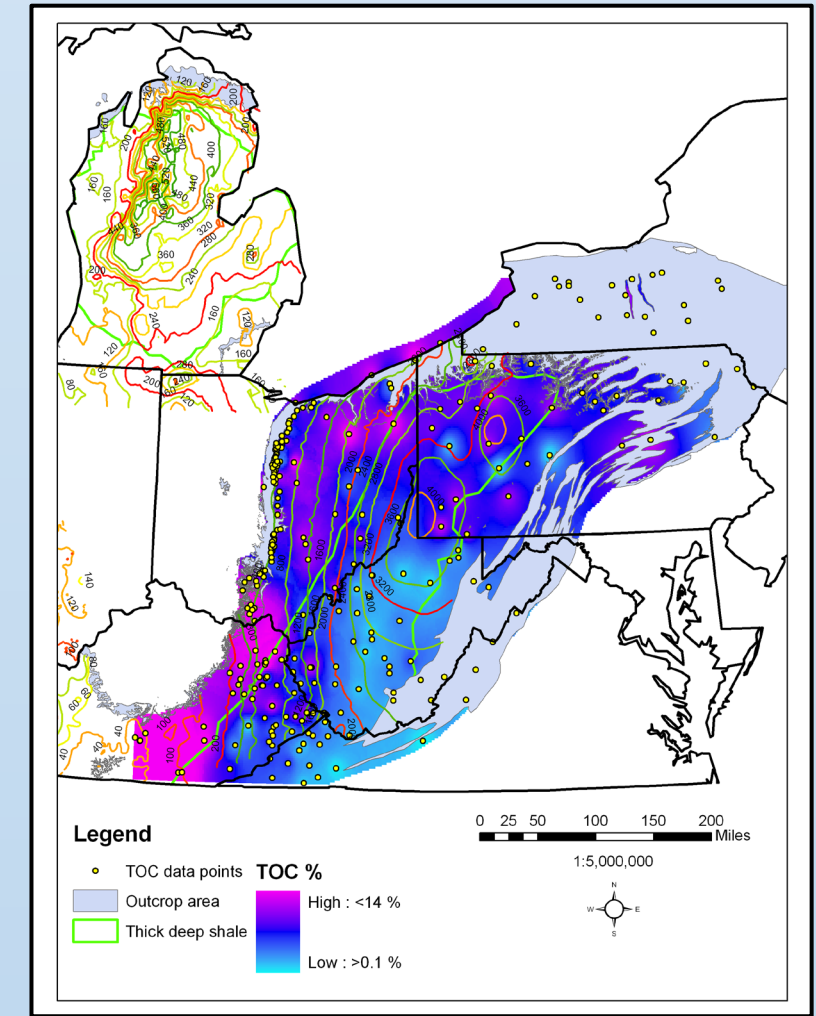
American Association of Petroleum Geologists  
Annual Convention and Exhibition  
San Antonio, Texas  
May 22, 2019

**ABSTRACT**

The potential for carbon storage and enhanced gas recovery in the Middle Devonian Marcellus and Upper Ordovician Utica organic-rich shales in the Appalachian Basin is being investigated using methods developed during investigation of the Upper Devonian Ohio Shale. Laboratory analysis of core and well cuttings provides baseline data for modeling TOC content in shale. In general, continuous resource plays exhibit relationships between measured TOC and wireline log data. TOC is in turn related to gas content and storage capacity. Wireline-based petrophysical models for estimating TOC have been proposed by many authors, but choice and application of a model depends on data availability. Only those based on total gamma-ray and bulk-density log data were used in this study, because they are most regionally available.

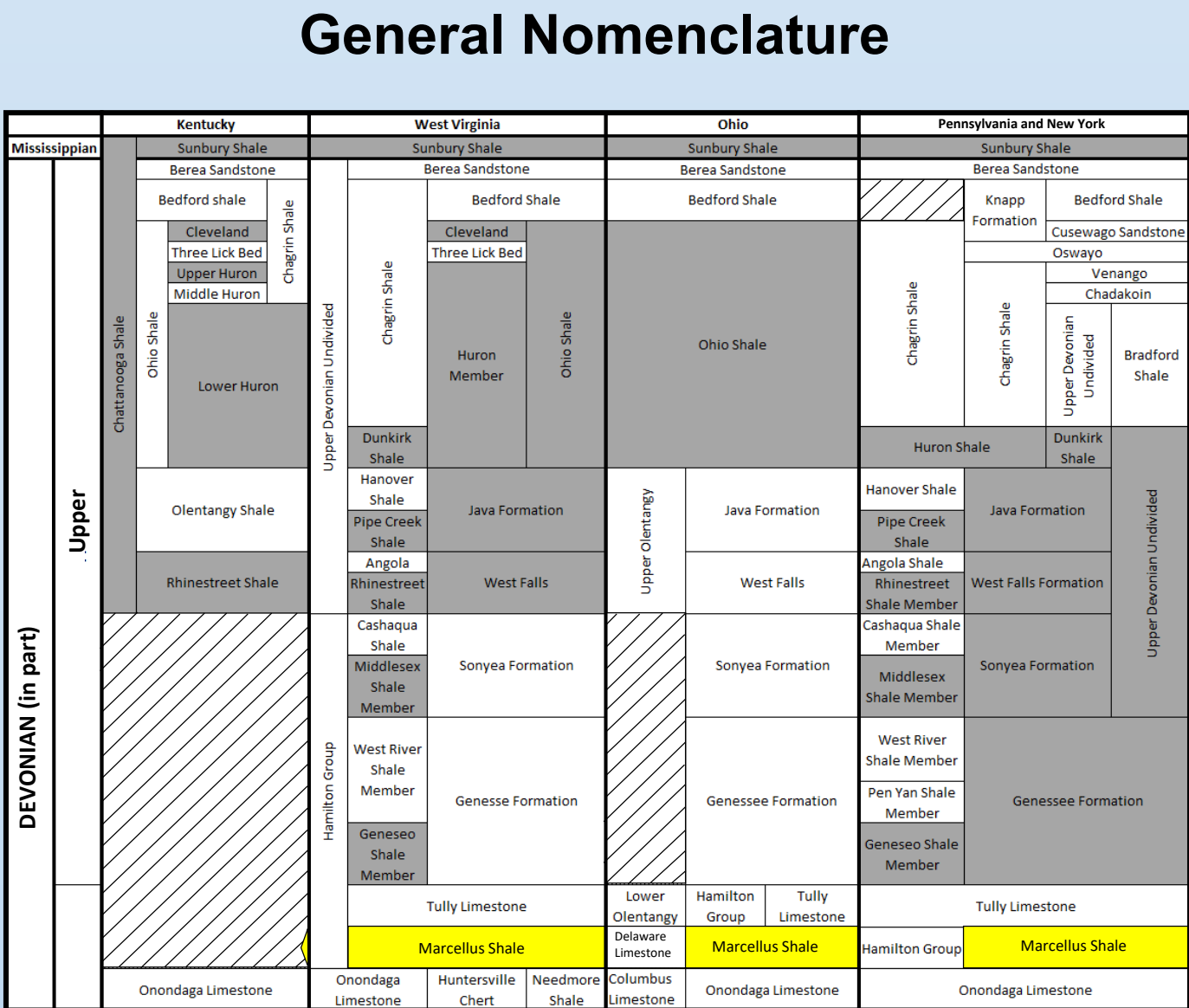
For the Marcellus, multiple models were analyzed to estimate TOC from log data. The simplest model for estimating TOC is a linear regression of a density and TOC cross plot based on laboratory data because TOC is generally regarded as the main control on density changes in an organic-rich shale. Gamma-ray- and density-based models use the slope of the gamma ray–density cross plot. A median TOC curve (P50) was calculated using multiple models to provide a probabilistic summary of TOC by well, which was used as input to geospatial modeling.

The Utica Shale was deposited in a carbonate-dominated open-marine shelf setting, suggesting that organic matter types and their mode of preservation differ significantly from those of the Marcellus. Classic models to estimate TOC for organic-rich shale may not provide acceptable results. Laboratory TOC and digital well-log data were compiled by the Utica Shale Consortium. Leco TOC data were depth-matched with gamma-ray and bulk-density data from logs. Neutron-porosity and photoelectric effect data were collected, but limited digital data precluded their use. Gamma-ray and density data were used to assess existing TOC models and formulate new ones. Two new models for calculating TOC from well-log data are proposed based on best-fit correlations to the distribution of laboratory TOC data.



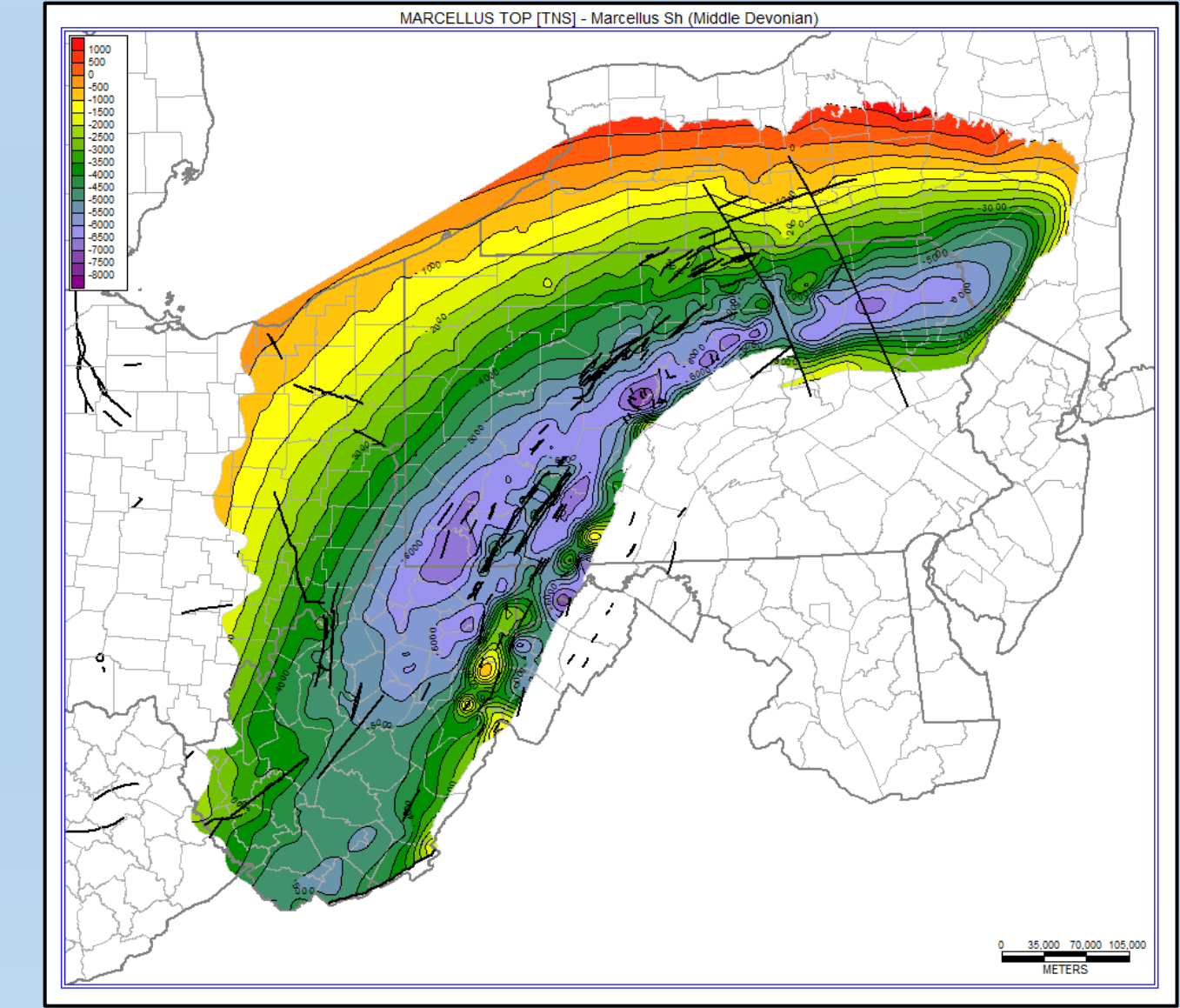
Original storage estimate

- “One size fit all” – 3D distribution of TOC not considered
- Digital well log data not incorporated
- Total Devonian Shale (including Marcellus)



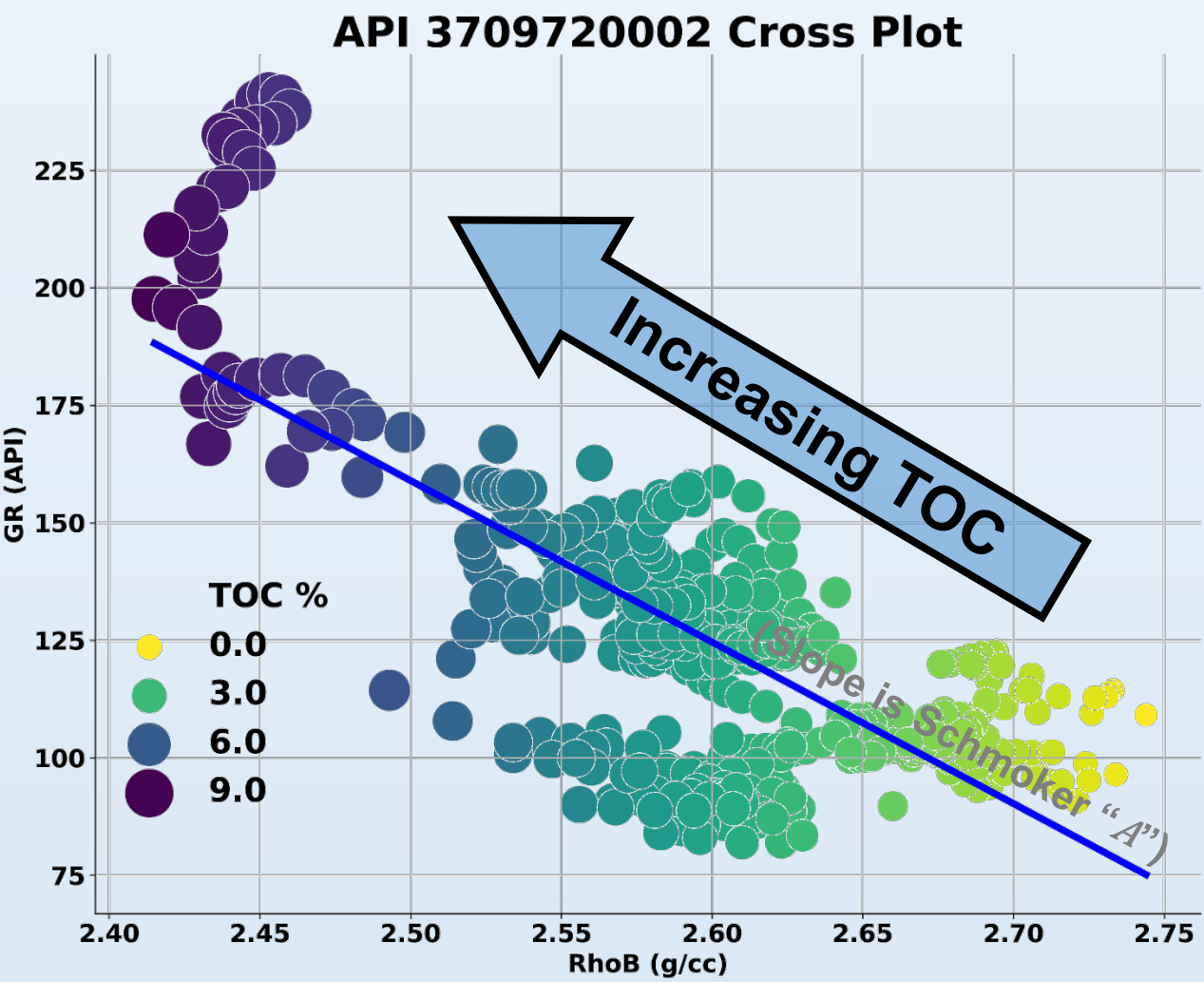
Correlation chart of the Middle and Upper Devonian. Black organic-rich shales are shaded gray. The Marcellus Shale is highlighted in yellow. Adapted from Patchen and others (1985), de Witt and others (1993), and Milici (1996).

Structure contour map on top of the Marcellus Shale

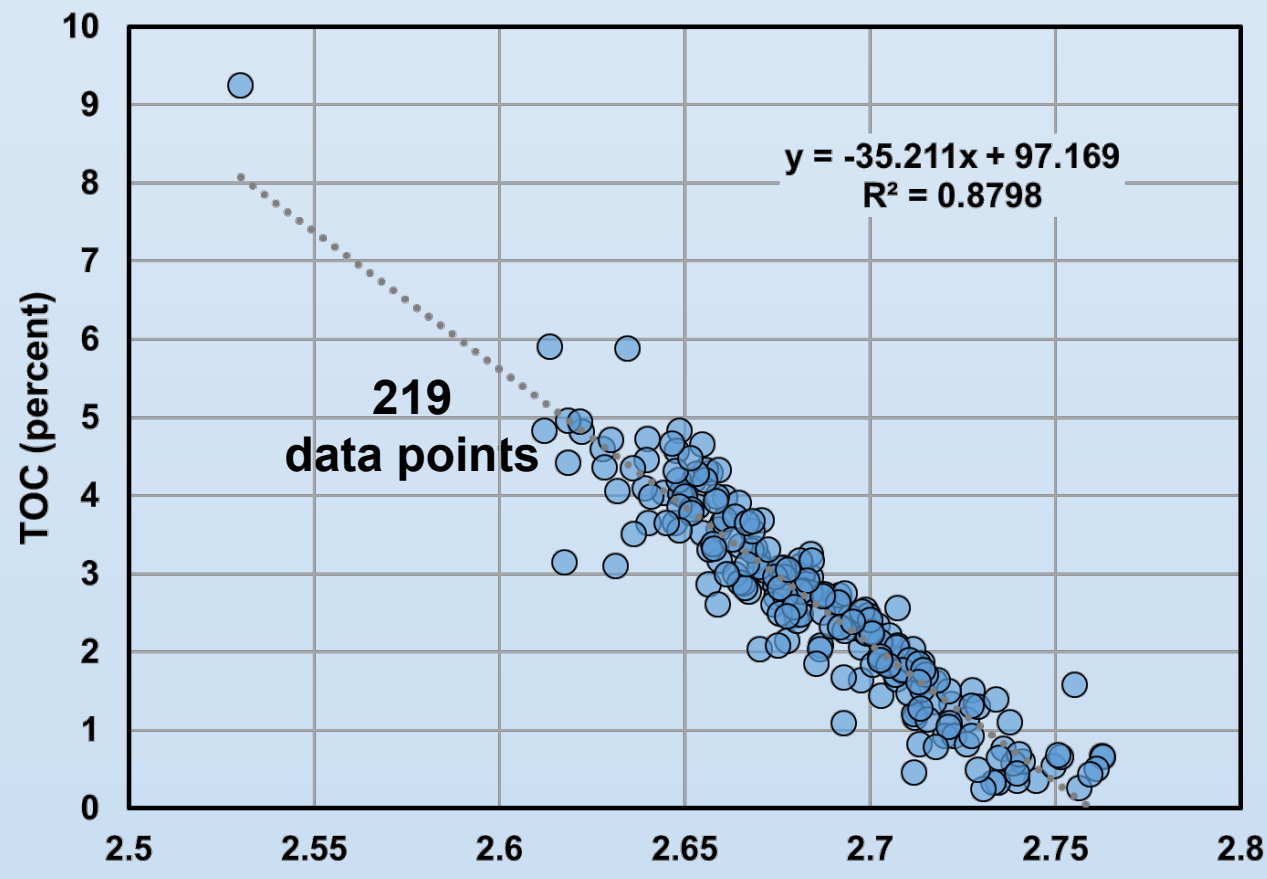


Funded by NETL/DOE  
Contract No: DE-FC26-05NT42589

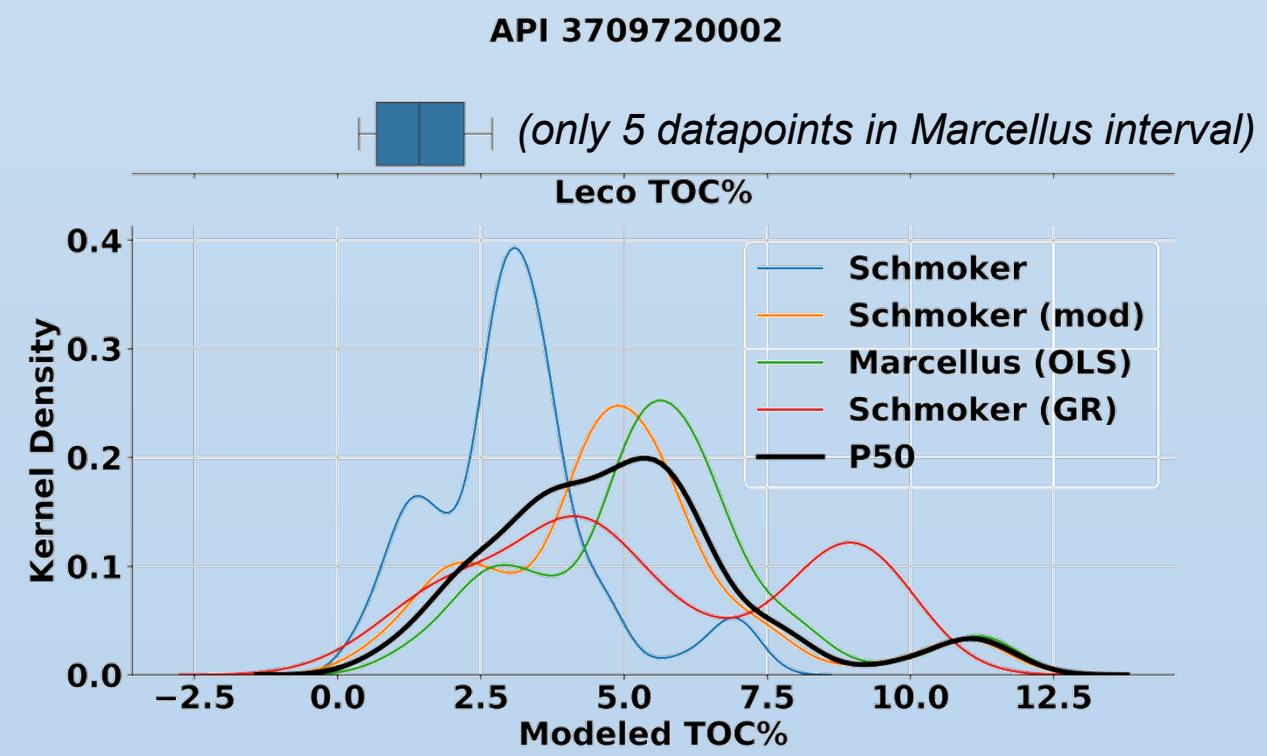
TOC is proportional to GR and inversely proportional to density



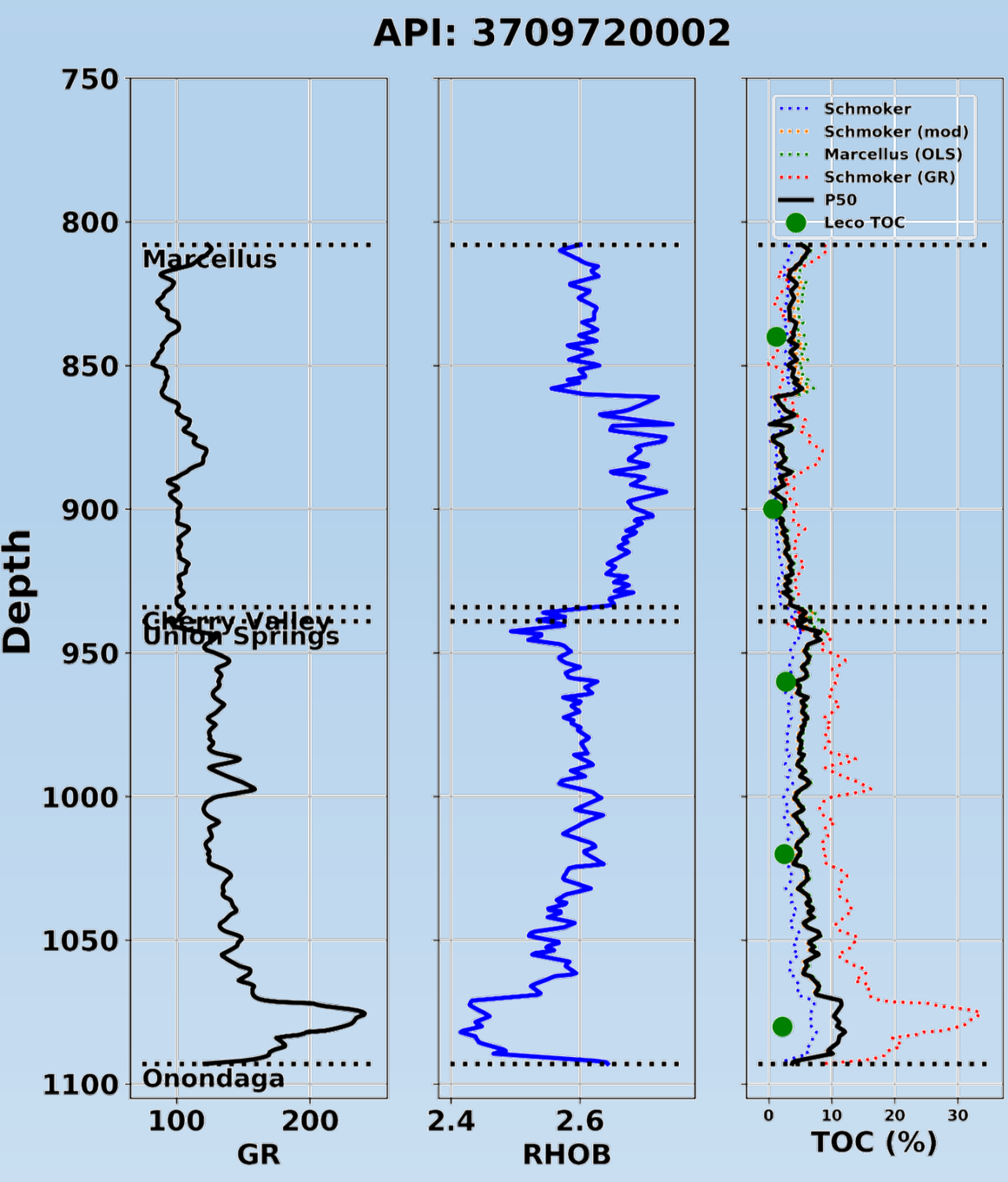
Leco TOC and laboratory density



Leco TOC compared to modeled TOC



Sample variation of calculated TOC logs and Leco TOC from samples



Models for determining TOC from wireline data

Basic idea is the TOC increases with increasing gamma ray intensity and is inversely proportional to density.

**Schmoker-based models**

$$TOC_{Sch} = 55.822 * \left( \frac{Rho_{max}}{RhoB} - 1 \right)$$

(Schmoker, 1979 & 1993)

$$TOC_{mod} = 88.55 * \left( \frac{Rho_{max}}{RhoB} - 1 \right)$$

(Modified Schmoker using linear solver to minimize RMSE between calculated and laboratory TOC.)

$$TOC_{GR} = \frac{(GR_{min} - GR)}{1.378 * A}$$

(Schmoker, 1981)

$$TOC_{OLS} = -35.21 * RhoB + 97.17$$

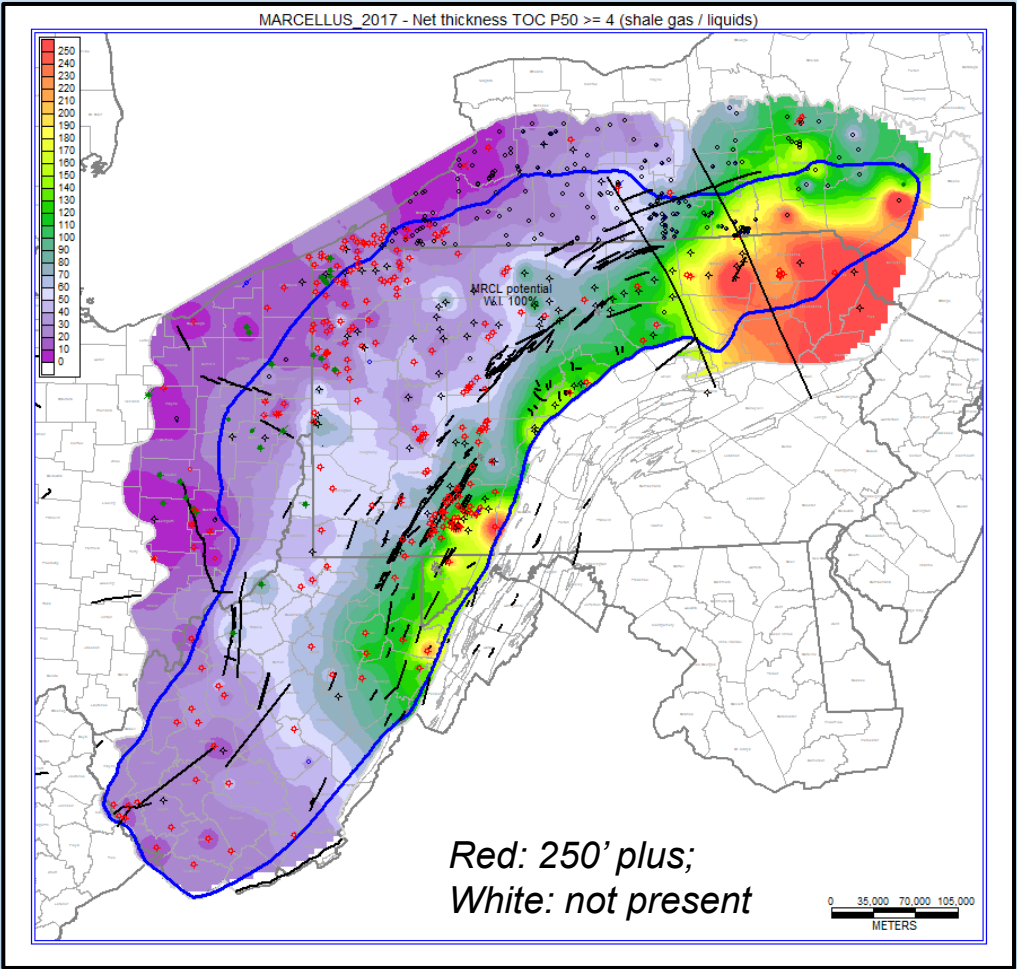
(Ordinary least squared regression of laboratory TOC and density data from the Pennsylvania shale data workbook.)

Method summary using gridded data developed by processing LAS files:

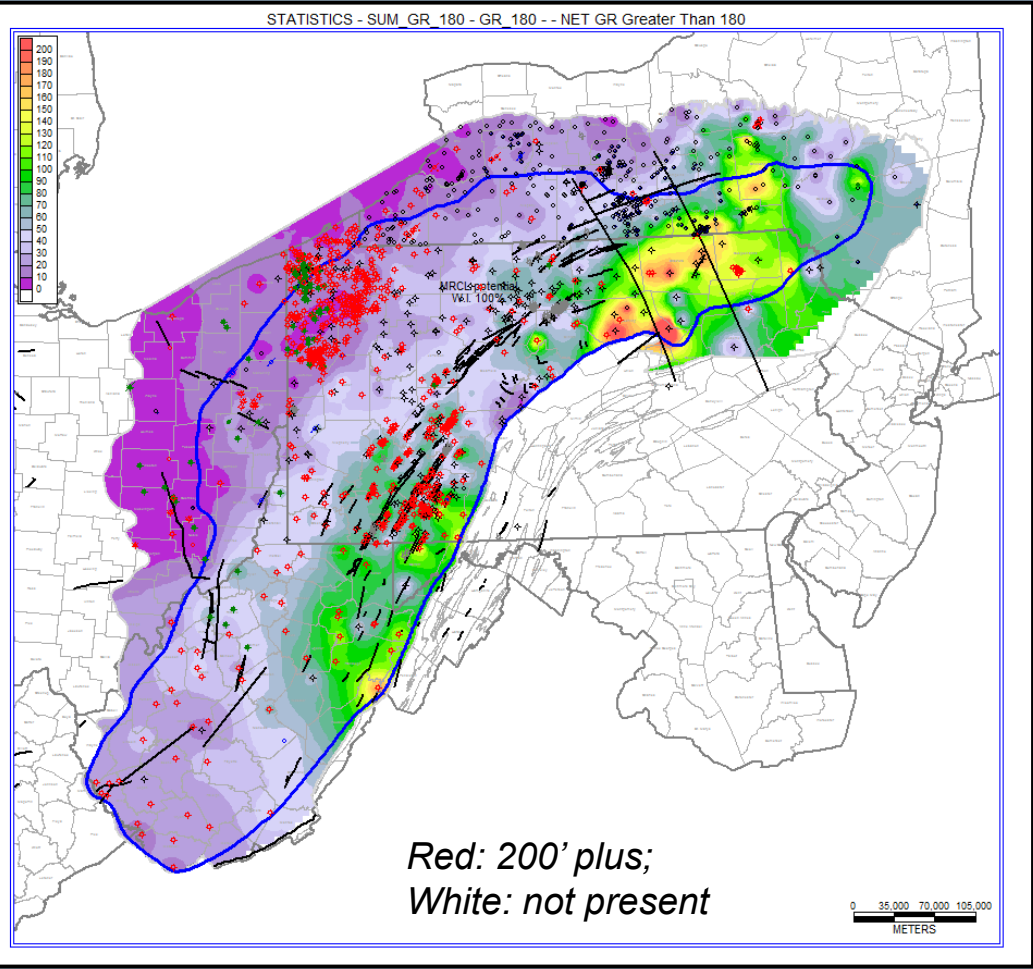
- $TOC=f(GR)$  or  $f(RhoB)$
- $S_{cfCO2}=f(TOC)$
- $Tons_{shale}=Area * thickness * RhoB$
- $Storage=Tons_{shale} * S_{cfCO2} * efficiency$

Caveats

1. Maximum bulk density,  $Rho_{max}$ , varies across region
2. Does not directly account for relationship between porosity and maturity



Gridded net thickness of organic-rich Marcellus Shale with TOC >= 4 % (shale gas / liquids potential), 575 wells.

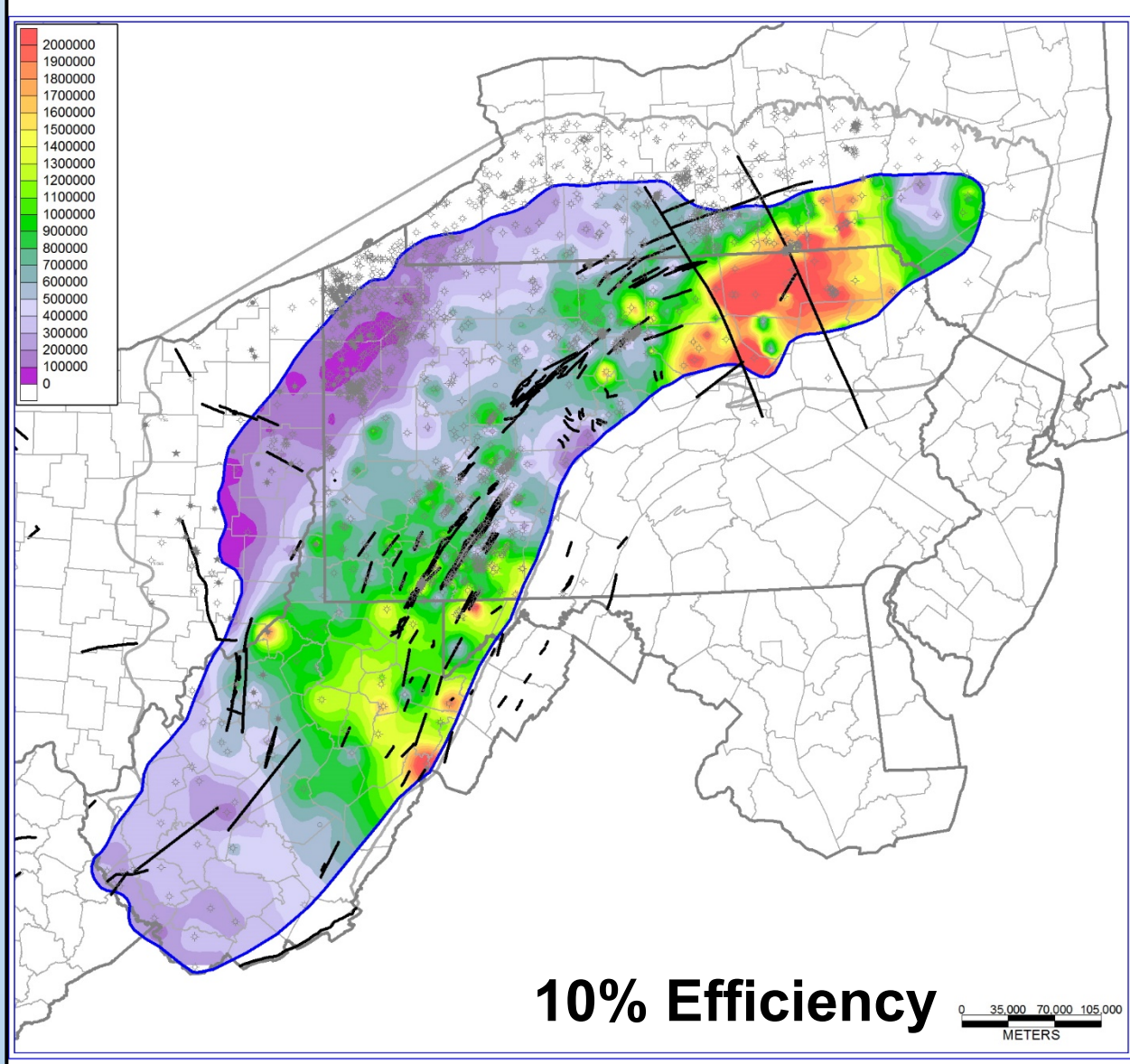
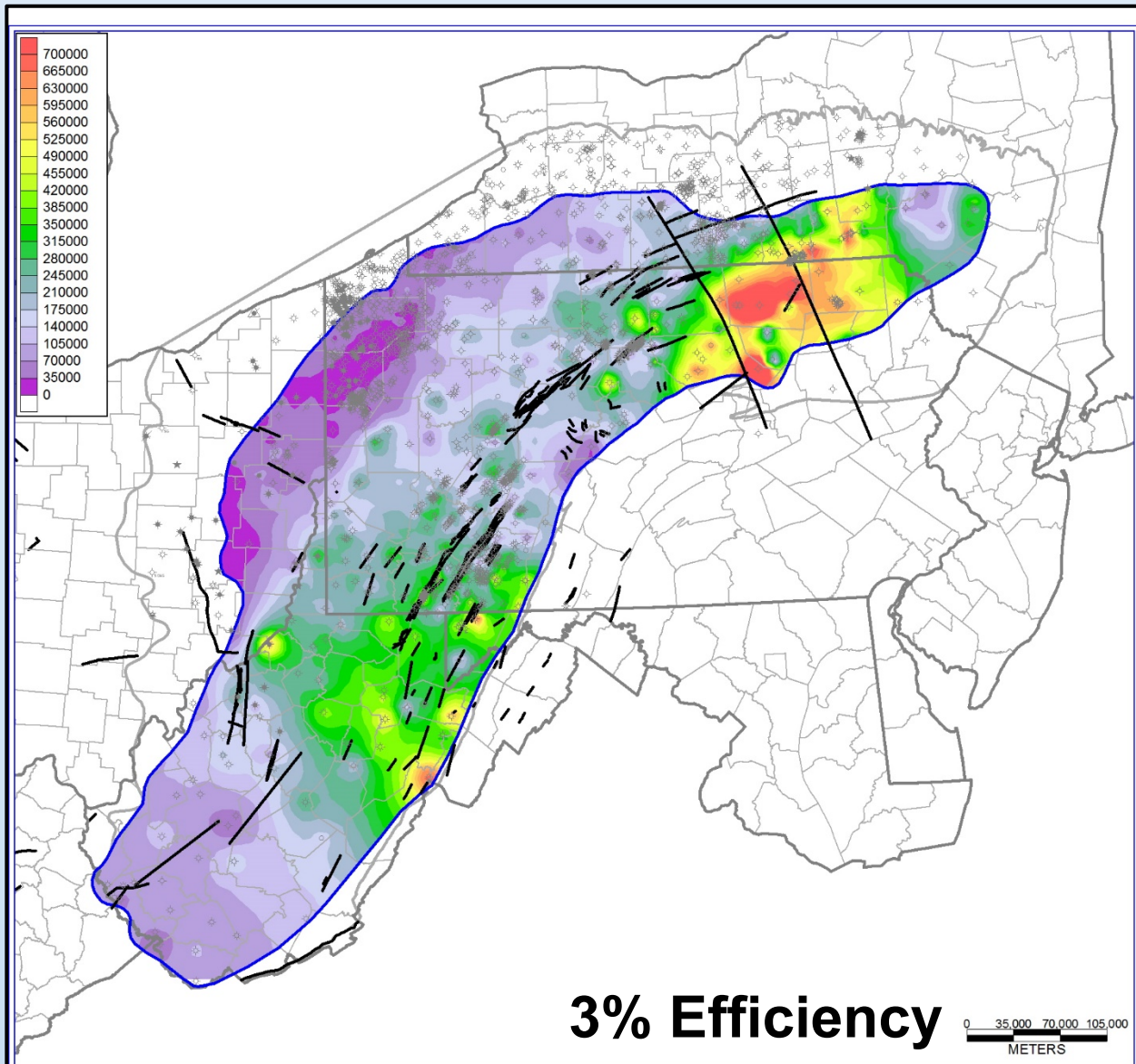


Updated net thickness of organic-rich Marcellus Shale. Computed on net gamma ray greater than 180 API calculated in 1559 wells.

Assessment acres

Assessment parameters	Total Area (Million Acres)	Assessment Area (Million Acres)	Average Thickness (Feet)	Volume (Million Acre-Feet)
TOC >= 2% Shale Source Rock Potential	36.45	36.41	90.44	3,292.9
TOC >= 4% Shale Gas/Liquids Potential	36.45	36.41	75.99	2,766.9

Storage distribution



Revised Marcellus assessment area outlined in blue is >2,500 ft. deep and net thickness with TOC >1.5%.

CO <sub>2</sub> Storage Marcellus Shale (million tons)		
State	3% Efficiency Factor	10% Efficiency Factor
Kentucky	0.88	2.92
Maryland	19.02	63.40
New York	124.31	414.36
Ohio	23.73	79.09
Pennsylvania	444.16	1,480.55
Virginia	0.35	1.17
West Virginia	274.07	913.55
Total	886.51	2,955.04

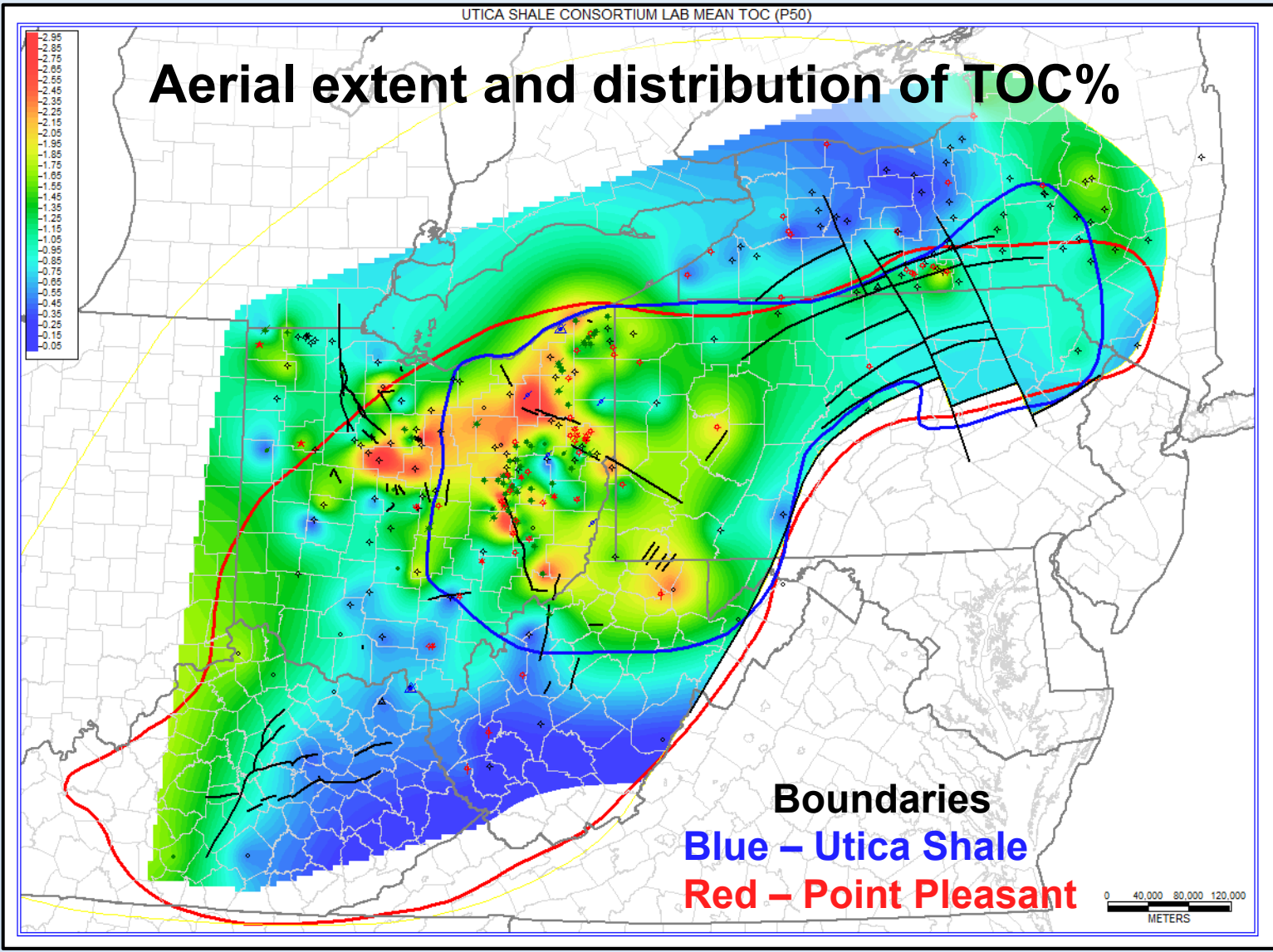
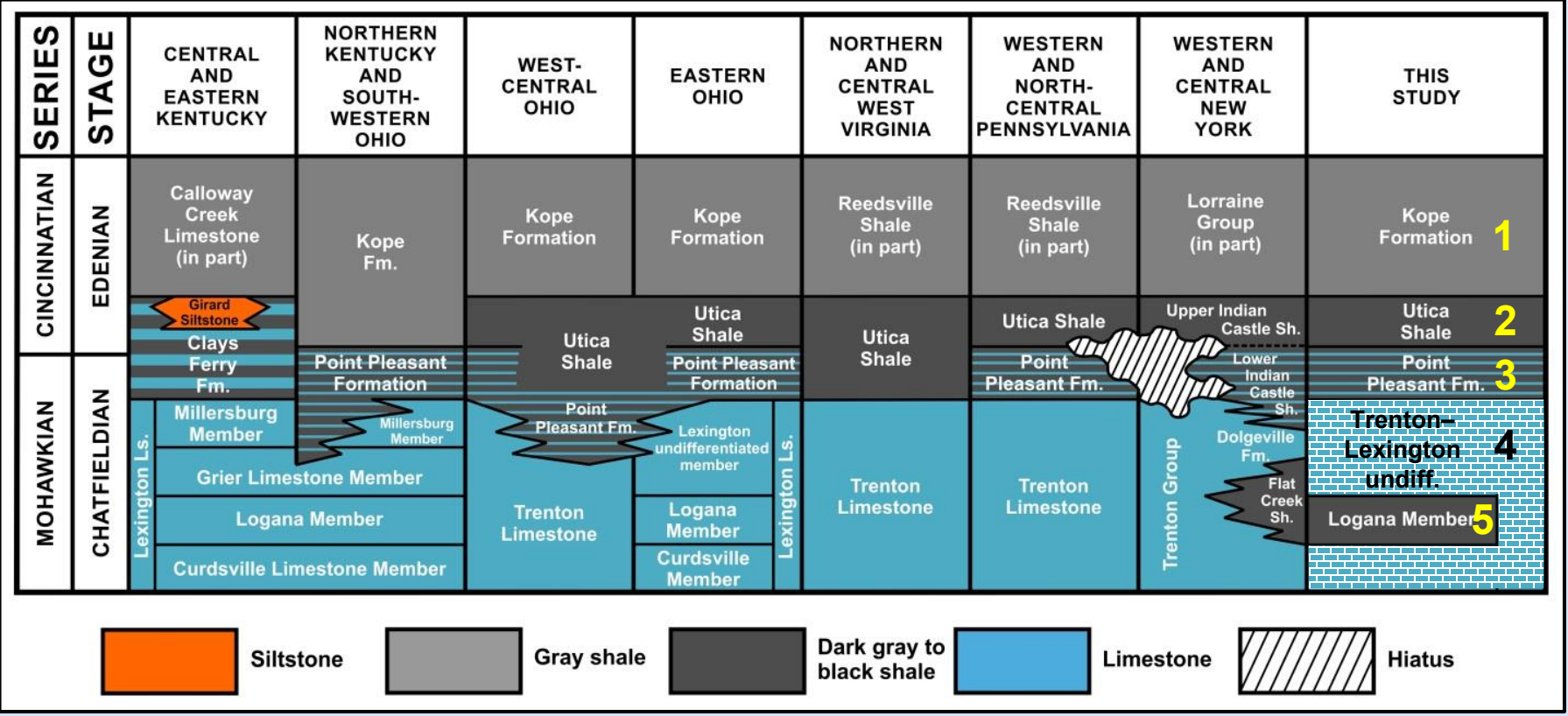


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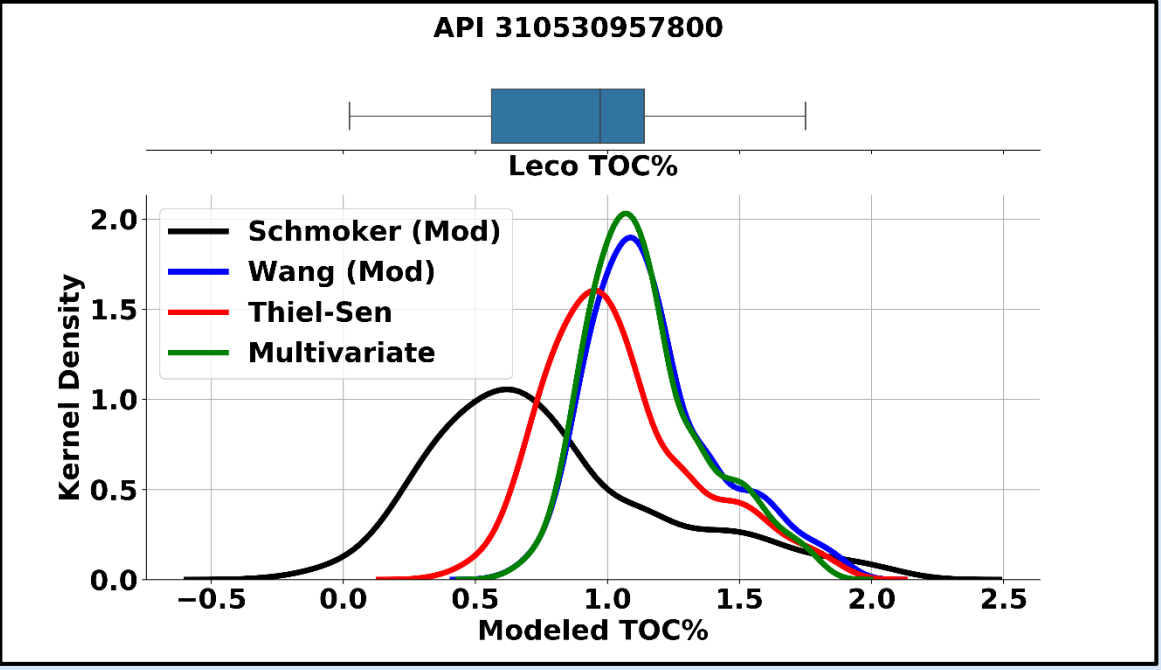
Utica Shale  
Point Pleasant

The Utica Research Consortium Play Book  
General Stratigraphy

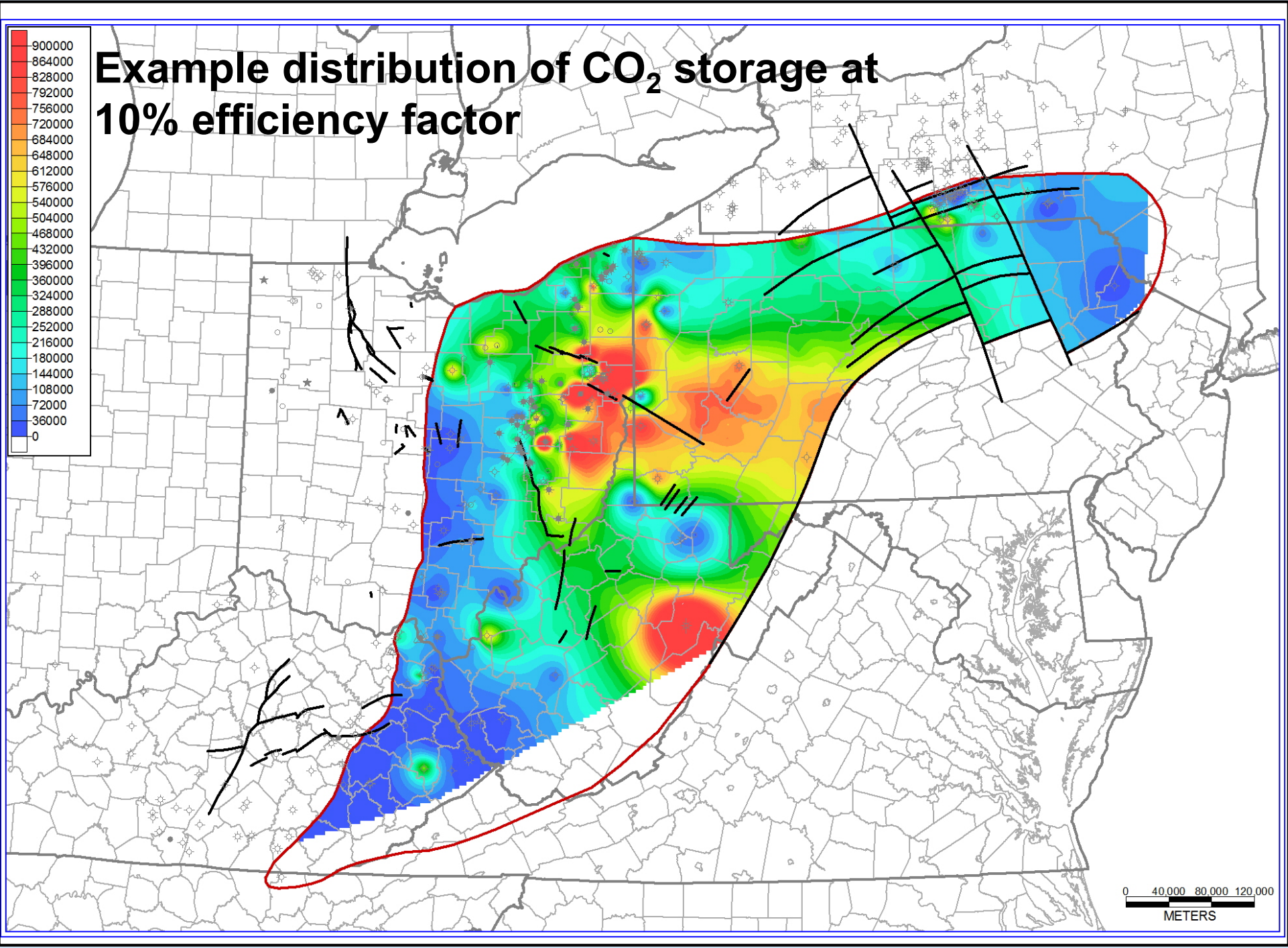
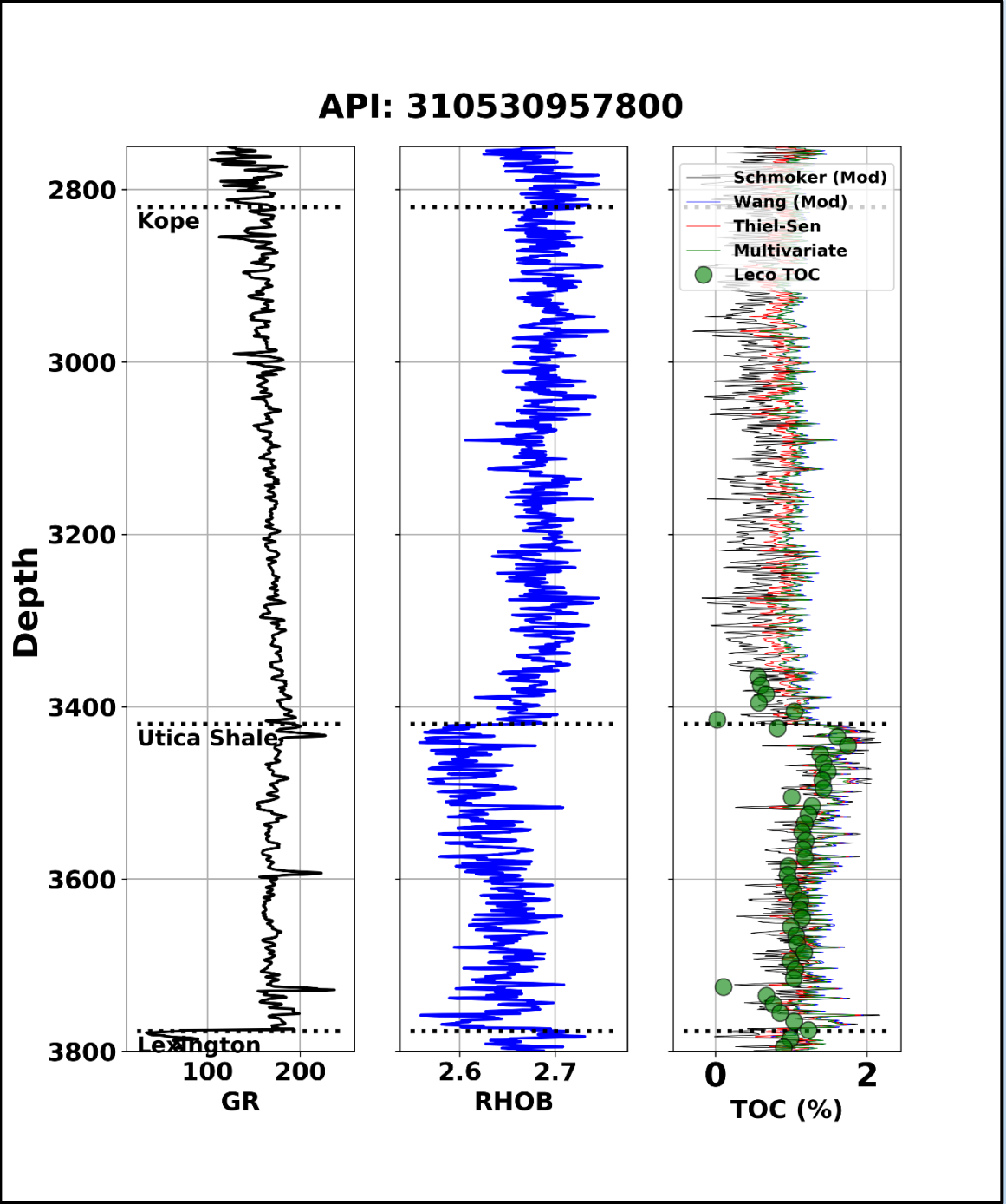


Adsorbed CO<sub>2</sub> associated with TOC

Distribution of Leco TOC (box plot) compared to calculated TOC (kernel density)



Leco TOC compared to calculated TOC from wireline data



CO <sub>2</sub> Storage at 3% Efficiency Factor (million tons)			
State	Utica Shale and Point Pleasant Combined		
	Adsorbed	Matrix	Total
Kentucky	0.56	22.93	23.48
Maryland	0.46	42.76	43.23
New York	0.71	45.95	46.66
Ohio	6.91	556.73	563.64
Pennsylvania	14.66	1,124.36	1,139.01
Virginia	0.01	0.49	0.49
West Virginia	6.72	524.35	531.07
Total	30.03	2,317.57	2,347.59

CO <sub>2</sub> Storage at 10% Efficiency Factor (million tons)			
State	Utica Shale and Point Pleasant Combined		
	Adsorbed	Matrix	Total
Kentucky	1.87	76.42	78.28
Maryland	1.55	142.54	144.09
New York	2.35	153.18	155.53
Ohio	23.05	1,855.77	1,878.82
Pennsylvania	48.86	3,747.86	3,796.72
Virginia	0.02	1.62	1.64
West Virginia	22.40	1,747.84	1,770.24
Total	100.09	7,725.23	7,825.32

Selected References

De Witt Jr., W., Roen, J.B., and Wallace, L.G., 1993, Stratigraphy of Devonian black shales and associated rocks in the Appalachian Basin, in Roen, J.B., and Kepferle, R.C., eds., Petroleum geology of the Devonian and Mississippian black shale of eastern North America, USGS Bulletin 1909, p.B1–B57.

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Nuttall, B.C., Drahovzal, J.A., Eble, C.F., and Bustin, R.M., 2009, Regional assessment of suitability of organic-rich gas shales for carbon sequestration: An example from the Devonian shales of the Illinois and Appalachian basins, Kentucky, in Grobe, M., Pashin, J.C., and Dodge, R.L., eds., Carbon dioxide sequestration in geological media—State of the science: AAPG Studies in Geology 59, p. 173–190.

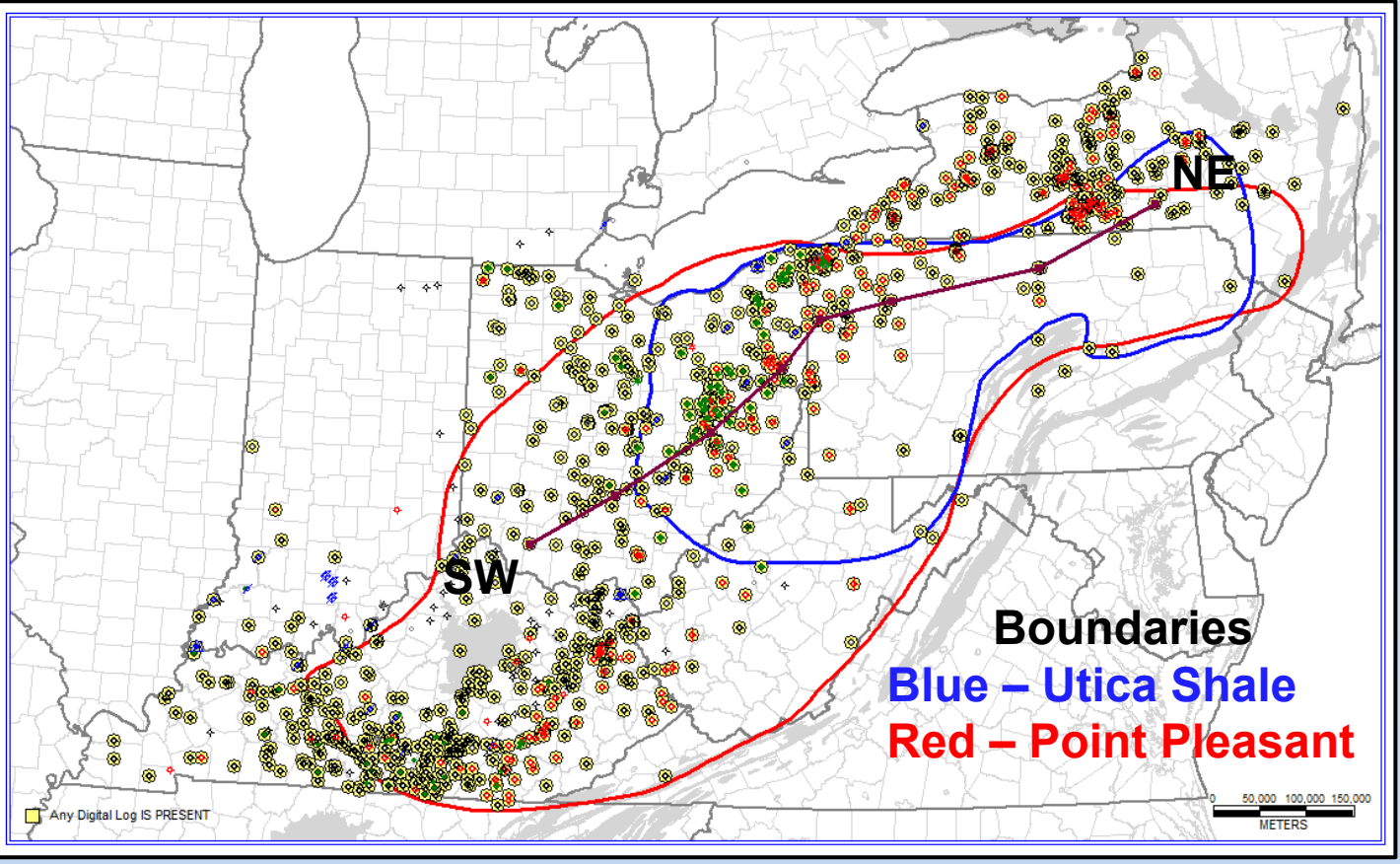
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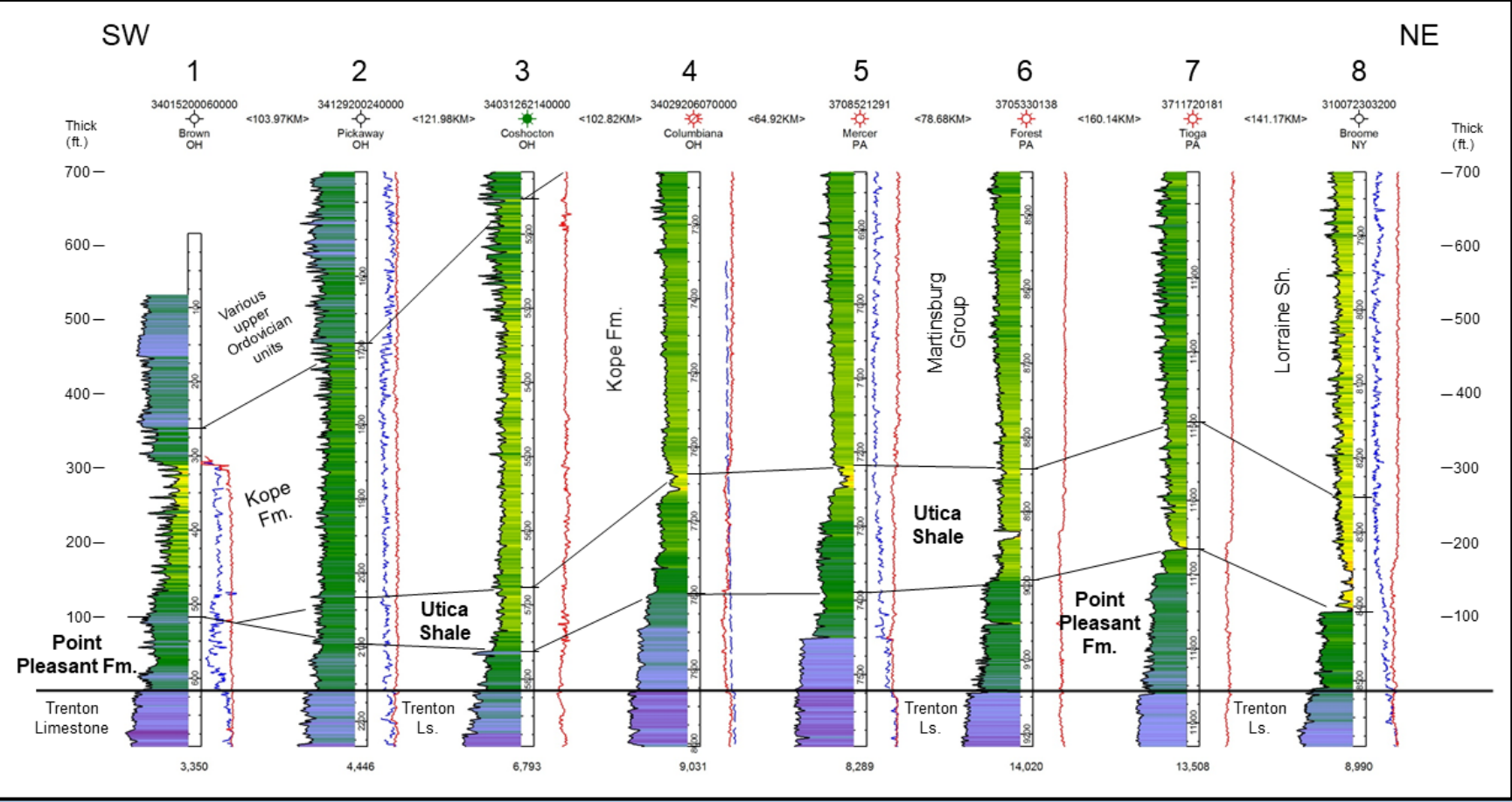
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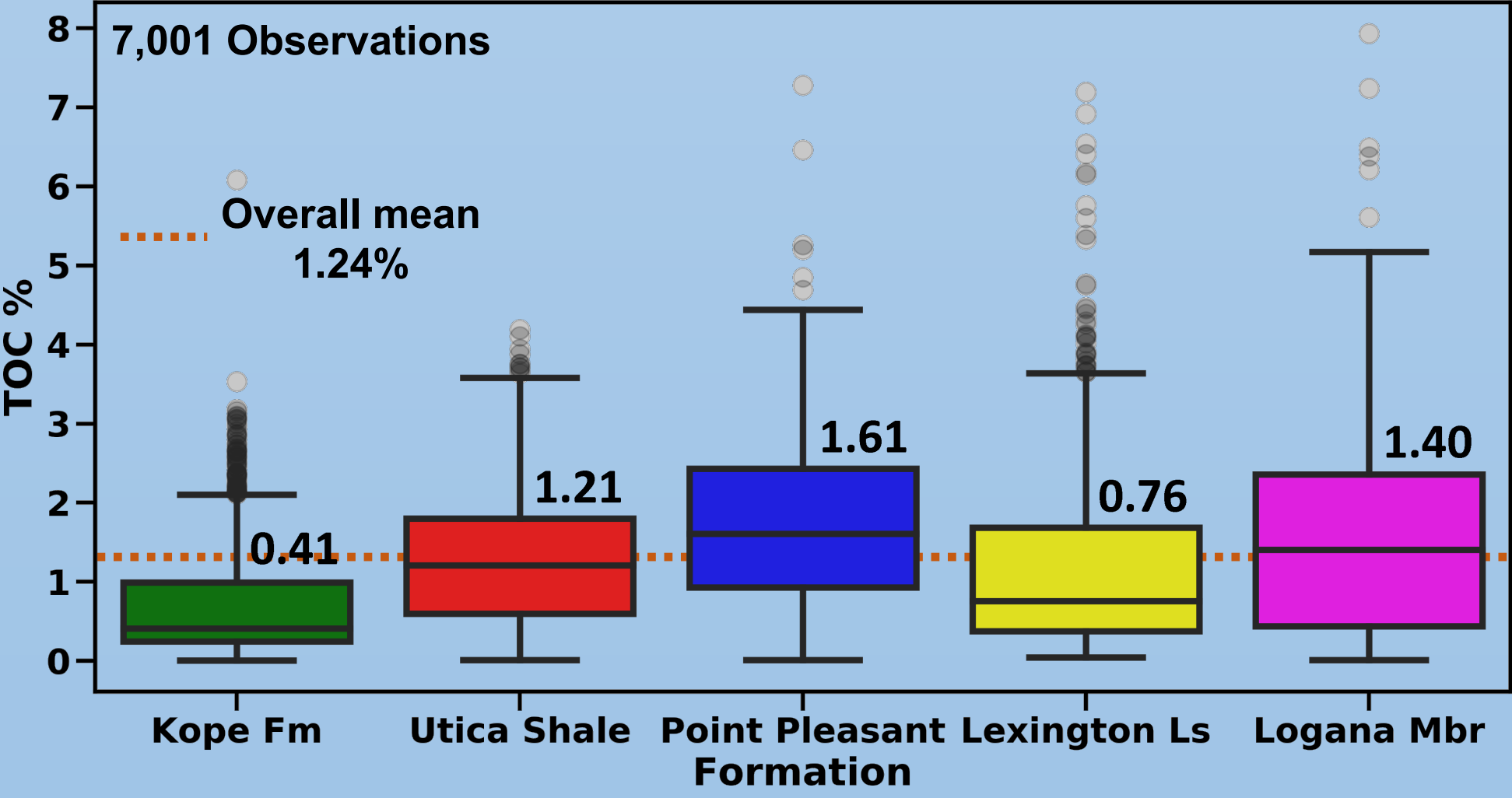
Extent of Utica Shale and Point Pleasant Formation



Stratigraphy varies across basin



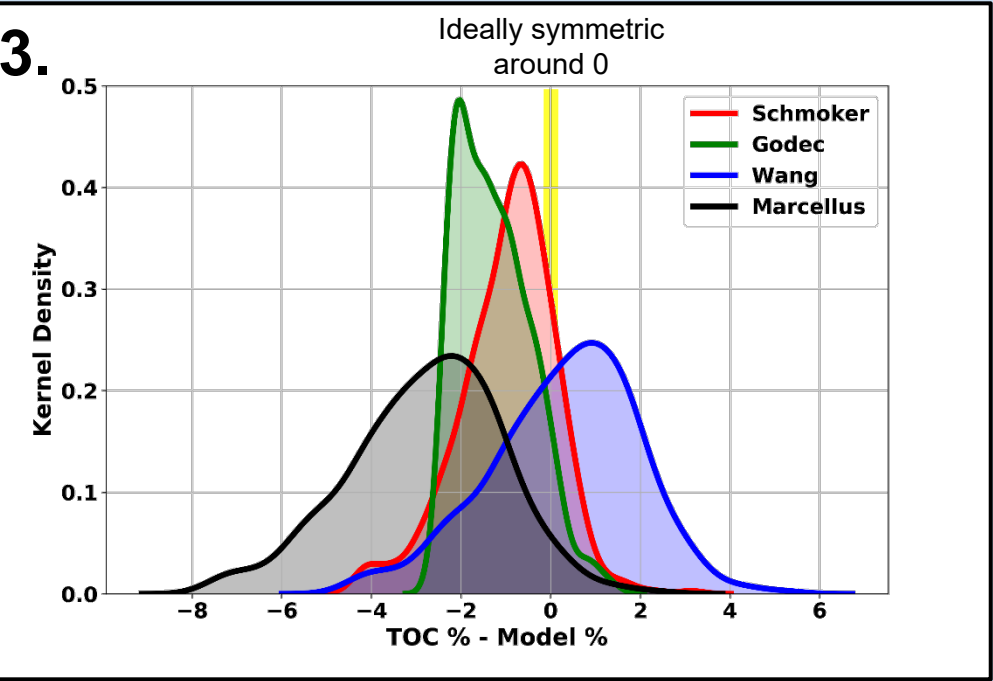
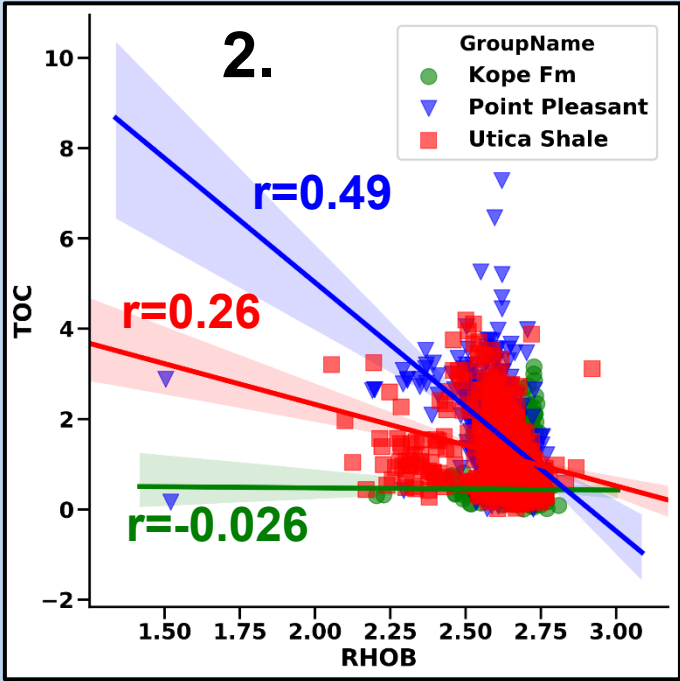
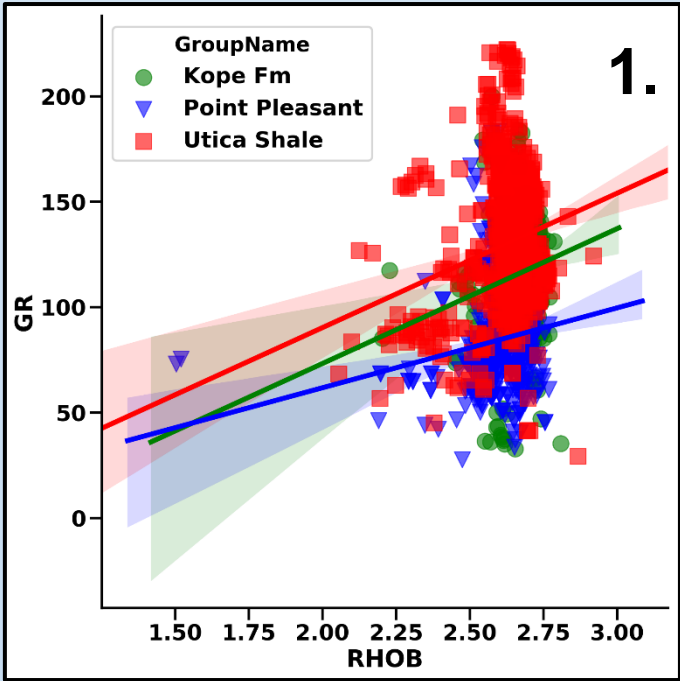
Distributions of TOC for selected Upper Ordovician units



The train-test split method divides a data set into two parts for training and testing. Parameters of a predictive model are computed using the training set. The goodness of fit is then checked against the test data. By performing this operation multiple times, goodness of fit parameters ( $r^2$  or RMSE) can be optimized.

Challenges

1. Density (RHOB) and gamma ray cross plots show little correlation.
2. Relationships of TOC to density (RHOB) are weak to moderate.
3. With classic models, distribution of residuals of Leco TOC to modeled TOC suggest they might not be optimum.

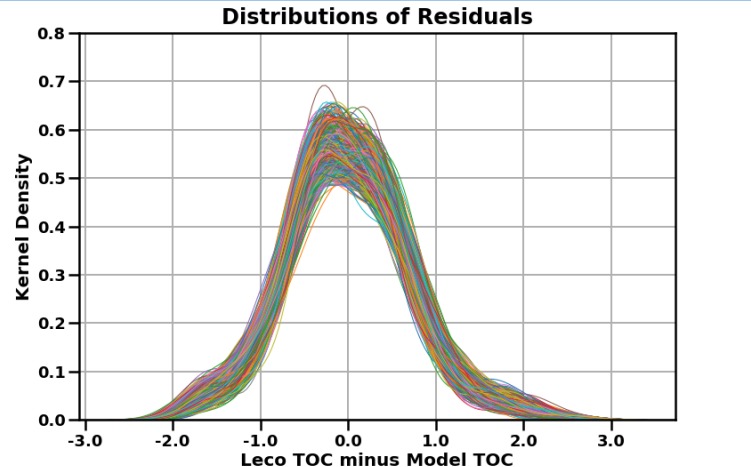


TOC Models Tested, most significant are shaded

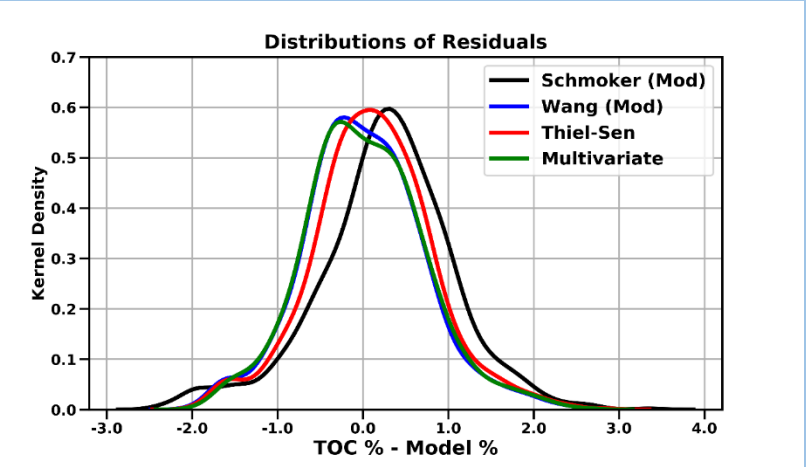
Model	Notes	$r^2$	RMSE
$TOC_{OLS}$	From Marcellus	-15.86	3.39
$TOC_{Wang} = \frac{(238.1)}{RhoB} - 89.1$	Wang and others (2016)	-4.32	1.90
$TOC_{Sch}$	From Marcellus	-1.21	1.23
$TOC_{Godec} = \frac{(RhoB - 2.73)}{-0.05}$	Godec (2013)	-0.98	1.16
$TOC_{SchUtica} = 32.5 * \left( \frac{2.73}{RhoB} - 1 \right)$	Minimize RMSE	-0.03	0.84
$TOC_{TS} = -8.137 * RhoB + 22.746$	Thiel-Sen regressor	0.25	0.71
$TOC_{WangMod} = \frac{(49.331)}{RhoB} - 17.327$	Minimize RMSE	0.28	0.70
$TOC_{MV} = 18.415 - 6.444 * RhoB - 0.00049 * GR$	Multi-variate Train-test split	0.41	0.58

$r^2$  is coefficient of determination (analogous to correlation coefficient)

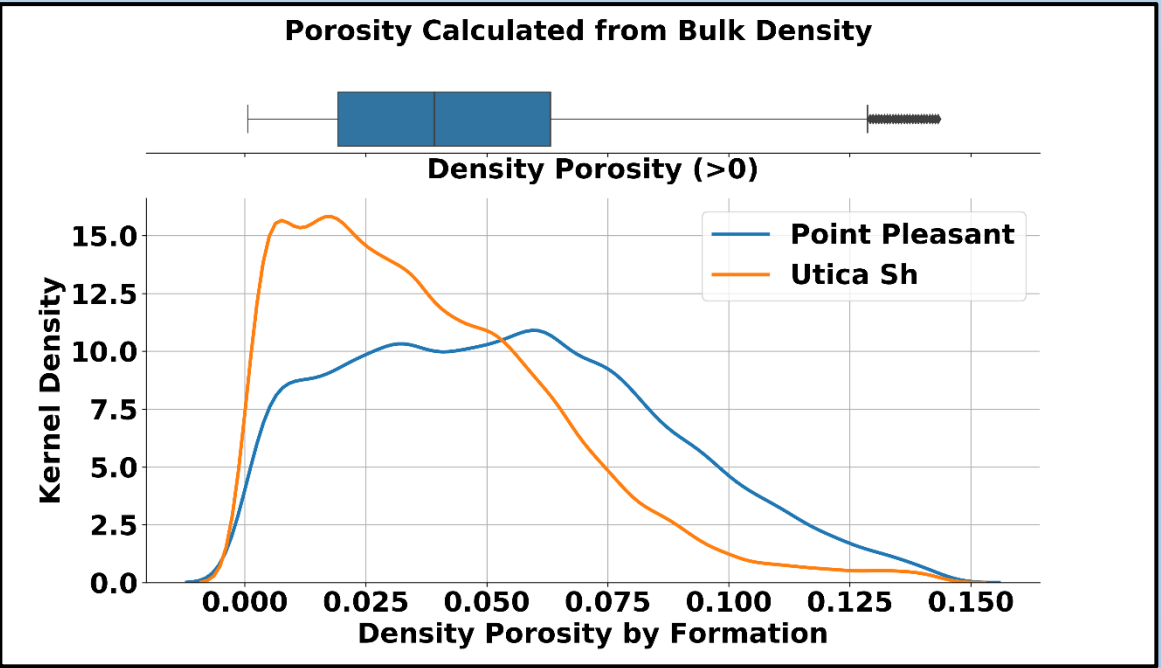
Residuals:  
Train-test split optimization for  $TOC_{MV}$



Updated models



Free Gas Stored in Matrix Porosity



Overall, the Point Pleasant has a larger extent and greater porosity so will have a larger storage capacity.

All CO<sub>2</sub> storage calculations are variations of: (illustration of storage in matrix porosity)

For each depth in the LAS file:

$$CO2_{matrix} = CO2_{Density@depth} * DPHI * (1 - S_w) * 0.5 * ef$$

For each well:

$$CO2_{tons/acft} = \frac{\sum CO2_{matrix}}{thickness}$$

For each formation:

$$CO2_{tons} = CO2_{gridded} * Thickness_{net} * Acres_{gridcell}$$



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