PS Noble Gas Isotopes, Major Element Isotopes, and Gas Composition from the Cumnock Formation: Sanford Sub-Basin, Deep River Basin, Lee County, North Carolina, U.S.A.*

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Editor's note: Please refer to relatively recent related articles by the principal author and associates: Search and Discovery Article #10612 (2014) and Search and Discovery Article #10662 (2014)

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Abstract

Noble gas isotopes, major element isotopes, and gas composition were obtained from the shut-in Butler #3 (API 32-105-00008) and Simpson #1 (API 32-105-00007) wells, drilled in 1998, and sample gas from the Cumnock Formation of Late Norian age. This is the first gas chemistry compilation of these wells. The wells' gas, sampled in 2009 and in 2014, had a strong 'fruity' light petroleum odor, a visible condensate plume when the wells were flowed, and are in the oil and wet gas window. Molecular and stable isotopic composition are typical of thermogenic natural gases; wetness and carbon and hydrogen isotopic composition of methane suggest generation in the oil window - consistent with the Cumnock's measured thermal maturity (%Ro= 0.8 – 1.0). Shut-in well pressures were ~900psi (Butler #3), and ~200psi (Simpson #1); both had a substantial initial gas flow. Limited data are from the 1982 Dummitt-Palmer #1 CBM well (API 32-105-00002), now plugged and abandoned.

Helium concentrations were ~0.20% to 0.24% from the noble gas analysis with neon ranging from 0.11 to 0.04 ppm and argon approximately 33 ppm. The measured noble gas composition contains very low atmospheric contamination with helium isotopes (0.07 R/RA) clearly defined by a crustal origin, while neon and krypton and are mainly attributed to atmospheric origin ($^{20}Ne/^{22}Ne$ ~9.8, $^{86}Kr/^{84}Kr$ ~0.3). Argon isotopes are mixed between crustal and atmospheric origins with $^{40}Ar/^{36}Ar$ values ~ 418 to 520. The $F^{20}Ne/^{36}Ar$ (~0.9 to 2.6), $F^{84}Kr/^{36}Ar$ (~0.8) and $F^{132}Xe/^{36}Ar$ (0.6–0.7) in the gas show enrichment in the light isotope associated with multi-stage fractionation processes with gas and fluid interaction.

The methane content (range ~58–64%) is inverse to the nitrogen content from denitrification of very thin ammonium-bearing units (also rich in oil), and likely from illite in overlying strata.

Selected References

Fulton, S,M., 1987, Geochemical analysis for The Chevron #1 Groce well, North Carolina (PDF), October 27, 1987, 32p.

Hoffman, C.W., and R.A. Beutel, 1991, The Dummitt-Palmer #1 coal bed methane test well, Lee County, North Carolina: North Carolina Geological Survey Open-File Report 91-1, 11p.

Helium Stewardship Act of 2013, Public Law 113-40---Oct. 2., 2013. Website accessed October 25, 2015, http://www.gpo.gov/fdsys/pkg/PLAW-113publ40/pdf/PLAW-113publ40.pdf.

Holmes, M., 1998, Petrophysical Report, Simpson No. 1 and Butler No. 3, Sanford Field, Lee County, North Carolina; prepared for Amvest Oil and Gas, Inc. by Digital Formation, Inc., Denver, Colorado (report located in North Carolina Geological Survey well files).

Krohn, M.D., J. Evans, and G.R. Robinson, Jr., 1988, Mineral-bound ammonium in black shales of the Triassic Cumnock Formation, Deep River basin, North Carolina, *in* A.J. Froelich, and. G.R. Robinson, Jr., editors, Studies of the Early Mesozoic Basins of the Eastern United States: U.S. Geological Survey Bulletin 1776, p. 86-98.

Kroos, B.M., R. Littke, B. Müller, J. Frielingsdorf, K. Schwochau, and E.F. Idiz, 1995, Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations: Chemical Geology, v. 126, p. 291-318.

Milici, R.C., J.L. Coleman, E.L Rowan, T.A. Cook, R.R. Charpentier, M.A. Kirschbaum, T.R. Klett, R.M. Pollastro, and C.J. Schenk, 2012, Assessment of undiscovered oil and gas resources of the East Coast Mesozoic basins of the Piedmont, Blue Ridge Thrust Belt, Atlantic Coastal Plain, and New England Provinces, 2011: U.S. Geological Survey Fact Sheet 2012–3075, 2 p. Website accessed October 25, 2015, http://pubs.usgs.gov/fs/2012/3075/.

Mingram [Plessen], B., P. Hoth, V. Lüders, and D.E. Harlov, 2005, The significance of fixed ammonium in Paleozoic sediments for the generation of nitrogen-rich natural gases in the North German basin. International Journal of Earth Sciences, v. 94/5-6, p. 1010-1022.

Littke, R., and B.M. Krooss, 2009, Unconventional Paleozoic gas resources in the German part of the Central European basin: AAPG European Region Annual Conference: Paris-Malmaison, France, p. 77-81 (extended abstract: AAPG Search and Discovery article #90099 (2009). Website accessed October 25, 2015, http://www.searchanddiscovery.com/pdfz/abstracts/pdf/2009/europe/abstracts/ndx_littke.pdf.html.

Olsen, P.E., D.V. Kent, J.H. Whiteside, J.C/ Reid, and K.B. Taylor, 2014, Chronostratigraphic context of the biotic assemblages of the Dan River-Danville and Deep River basins (Newark Supergrop, Virginia and North Carolina, USA: Southeastern Section annual meeting of the Geological Society of America, Abstracts with Programs, v. 46/3, p. 20. Website accessed October 25, 2015, https://gsa.confex.com/gsa/2014SE/webprogram/Paper237388.html

Olsen, P.E., J.C. Reid, K.B. Taylor, J.H. Whiteside, and D.V. Kent, 2015, Revised stratigraphy of the Late Triassic age strata of the Dan River basin (Virginia and North Carolina, USA) based on drill core and outcrop data: Southeastern Geology, v. 51/1, p. 1-31.

Reid, J.C., and R.C. Milici, 2008, Hydrocarbon source rocks in the Deep River and Dan River Triassic basins, North Carolina: U.S Geological Survey Open-File Report 2008-1108, 28p.

Reid, J.C., K.B. Taylor, and K.N.S. Cumberbatch, 2010, Digital compilation map Sanford sub-basin, Deep River basin, parts of Lee, Chatham and Moore counties, North Carolina [Seismic lines, drill hole locations, geologic units (from Reinemund, 1955), hydrocarbon shows (gas, oil, asphaltic - or combination) and %Ro in wells - Area within dotted line inferred extent of %Ro ≥ to 0.8].

Reid, J.C., and K.B. Taylor, with contributions by P.E. Olsen, and O.F. Patterson, III, 2011, Natural Gas Potential of the Sanford sub-basin, Deep River basin, North Carolina, 57p., *in* K.B. Taylor, and J.C. Reid, editors, Field Trip Guidebook – 60th Annual Meeting, Southeastern Section, Geological Society of America, Wilmington, North Carolina, March 2011. Note: updated and revised version of this field trip guidebook was prepared for the 2011 annual meeting of the Eastern Section, AAPG; Search and Discovery Article #10366 (2011). Website accessed October 25, 2015, http://www.searchanddiscovery.com/documents/2011/10366reid/ndx_reid.pdf.

Reid, J.C., M.M. McGlue, and G.S. Ellis, 2014a, Porosity, permeability, and pore characterization of the Triassic Cumnock Formation: A continuous gas assessment unit, Sanford Sub-Basin, Deep River Basin, Lee County, North Carolina, USA: Search and Discovery Article #10612 (2014). Website accessed October 25, 2015, http://www.searchanddiscovery.com/documents/2014/10612reid/ndx_reid.pdf.

Reid, J.C., K.B. Taylor, and M.M. McGlue, 2014b, Porosity, permeability, and pore characterization of the Triassic Cumnock Formation: A continuous gas assessment unit, Sanford Sub-Basin, Deep River Basin, Lee County, North Carolina, USA, Part 2: Search and Discovery Article #10662 (2014). Website accessed October 25, 2015, http://www.searchanddiscovery.com/documents/2014/10662reid/ndx_reid.pdf.

Reinemund, J.A., 1949, Geology of the Deep River Coal Field. Chatham, Lee and Moore counties, North Carolina: U.S. Geological Survey, Preliminary Map (in two sheets).

Reinemund, J.A., 1955, Geology of the Deep River coal field, North Carolina: U.S. Geological Survey Professional Paper 246, 159p.

Schruben, P.G., R.E. Arndt, and W.J. Bawiec, 1998, Geology of the conterminous United States at 1:2,500,000 scale - a digital representation of the 1974 P. B. King and H. M. Beikman map: USGS Data Series 11, 1 CD.

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Abstract

Noble gas isotopes, major element isotopes, and gas composition were obtained from the shut-in Butler #3 (API 32-105-00008) and Simpson #1 (API 32-105-00007) wells, drilled in 1998, and sample gas from the Cumnock Fm. of Late Norian age. This is the first gas chemistry compilation of these wells. The wells' gas, sampled in 2009 and in 2014, had a strong 'fruity' light petroleum odor, a visible condensate plume when the wells were flowed, and are in the oil and wet gas window. Shut-in well pressures were ~900 psi (Butler #3), and ~200 psi (Simpson #1); both had a substantial initial gas flow. Limited data are from the 1982 Dummitt-Palmer #1 CBM well (API 32-105-00002), now plugged and abandoned.

Helium concentrations were ~0.20% to 0.24% from the noble gas analysis with neon ranging from 0.11 to 0.04 ppm and argon approximately 33 ppm. The measured noble gas composition contains very low atmospheric contamination with helium isotopes (0.07 R/RA) clearly defined by a crustal origin, while neon and krypton and are mainly attributed to atmospheric origin ($^{20}Ne/^{22}Ne$ ~9.8, $^{86}Kr/^{84}Kr$ ~0.3). Argon isotopes are mixed between crustal and atmospheric origins with $^{40}Ar/^{36}Ar$ values ~ 418 to 520. The $F^{20}Ne/^{36}Ar$ (~0.9 to 2.6), $F^{84}Kr/^{36}Ar$ (~0.8) and $F^{132}Xe/^{36}Ar$ (0.6-0.7) in the gas show enrichment in the light isotope associated with multi-stage fractionation processes with gas and fluid interaction.

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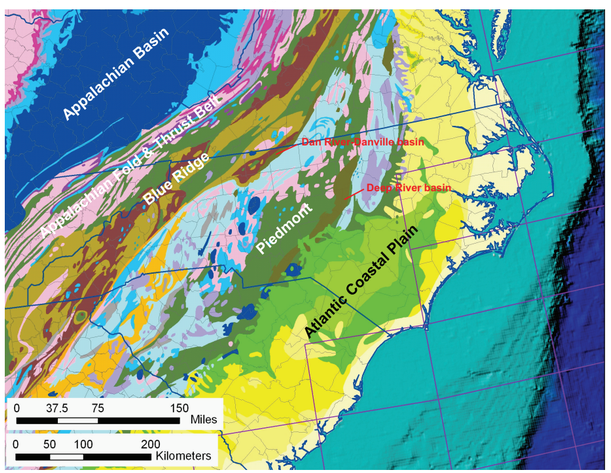
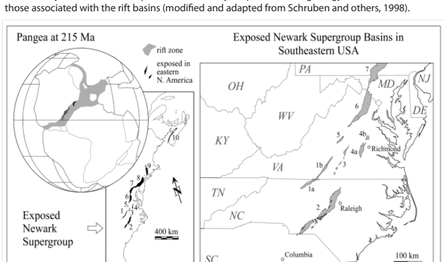
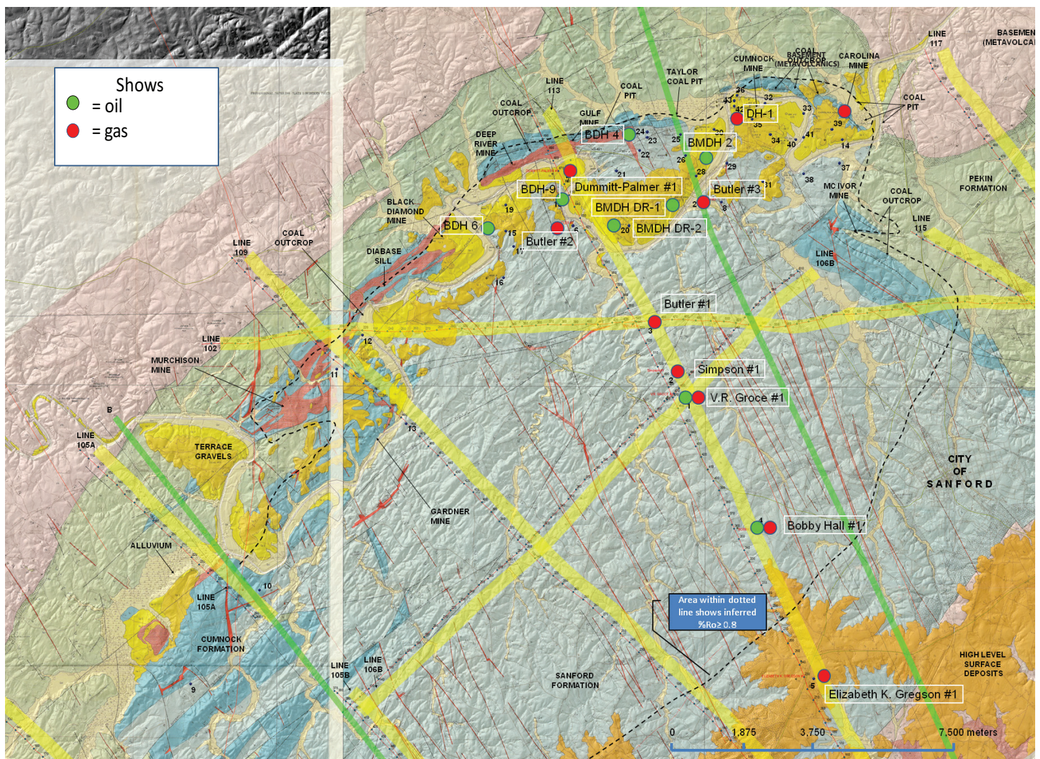


The geology of eastern North Carolina consists of a relatively thin to increasingly thick veneer of coastal plain sediments and sedimentary rocks of the Atlantic Coastal Plain, which range in age from Upper Jurassic (?) to Recent. These strata overlie a complex folded and faulted geology of metaigneous and metasedimentary rocks of Early Paleozoic to Late Proterozoic age, which in turn are punctuated in places by narrow Late Triassic (?) to Early Jurassic (?) rift basins. The stratigraphic geology of the Atlantic Coastal Plain section is composed of Mesozoic and Cenozoic siliciclastic and carbonate sedimentary rocks. This coastal plain has a relatively simple structural geology, with few faults and structures, other than those associated with the rift basins (modified and adapted from Schruben and others, 1998).



Exposed Newark Supergroup basins in the Southeastern USA (from Olsen and others, 2015). The Deep River basin is labeled 2; the Dan River basin is labeled 1 (includes 1a, 1b).

Panel 1 - Geologic and sub-surface setting



The Butler #3 and Simpson #1 wells are both shut-in. The gas from these two wells is the focus of this presentation. This map also shows the locations of other oil and gas wells, 2D dynamite-sourced seismic lines (yellow lines), and green lines are cross section lines in Reinemund (1955). The unlabled map area that is pink or uncolored is metavolcanic Paleozoic bedrock (adapted from Reid and others, 2010). Topography is from statewide LiDAR data (see hillshade in upper left. without geology draped on it).

Helium and other gases

Hydrogen sulfide and carbon dioxide were not detected in either well. "Wet ends" (ethane, ethylene, propane, iso-butane, n-butane, n-pentane, and hexanes+) are present in measurable quantities in both wells. Heavier carbon molecules are present in sub-percent quantities. Similar data for the Dummitt-Palmer #1 well are not available.

Helium was measured in 2009 in both wells at a concentration of about 0.218 mol. % (Butler #3) and 0.223 mol. % (Simpson #1) (Reid and others, 2011). In 2015 helium concentrations were ~0.20% to 0.24% along with neon ranging from 0.11 to 0.04 ppm and argon approximately 33 ppm (this contribution). The Cumnock Fm. natural gas helium content is just below the $3/10^{th}$ of 1 percent helium concentration, that can be economically extracted (Federal Helium Program, 2013).

The 'Helium Stewardship Act of 2013' has a provision for 'low-Btu gas separation and helium conservation'. This Act may lead to further evaluation of the potential helium resources in the Deep River basin. The Act "Authorizes the Secretary of Energy to support research, development, commercial application, and conservation to expand domestic production of low-Btu gas and helium resources; separate and capture helium; develop advanced membrane technology to separate low-Btu gases; develop technologies for separating, gathering, and processing helium in low concentrations; develop low-cost technologies and technology systems for recycling, reprocessing, and reusing helium; and develop industrial gathering technologies to capture helium from other chemical processing." (Helium Stewardship Act of 2013, Sec. 16, 17). It also authorizes a national helium gas assessment by the U.S. Geological Survey that quantifies crude helium resources…."

While no helium and noble gas analyses are available for the Dan River basin, there is no reason not to expect them based on the Deep River basin analyses.

Notes:

The Butler #3 and Simpson #1 wells were drilled in 1998, and the wells have been shut-in since then. Both wells had substantial initial gas flow, considerable initial gas pressures, and both maintain muchof their original gas pressure today. Perforations are shown by red-filled dots. Symbol position is close to actural perforation locations.

Butler #3 - According to the mud log, the contact between the Sanford Fm. and Cumnock Fm. is ~1,910 feet. Three intervals of the Sanford Fm. have a "trace of yellow cut." Two yellow cuts (one rated good), were noted in the mudlog in the Cumnock Fm. The contact between the Cumnock Fm. and the stratigraphically lower Pekin Fm. is at about ~2,540 feet. The well's inital flow rate is unknown.

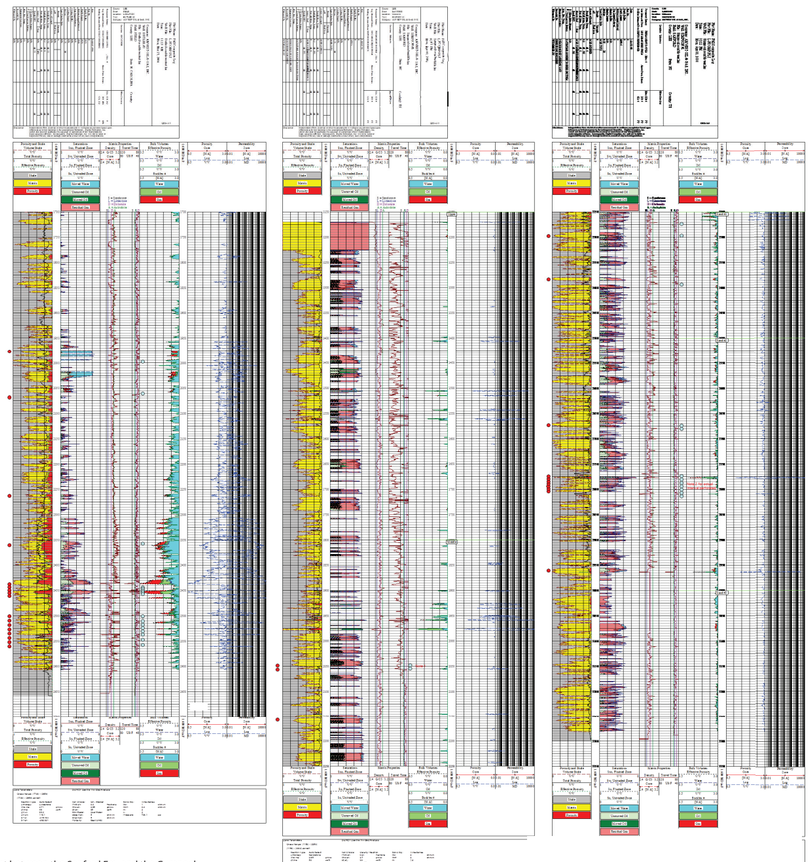
Since 2009, the Butler #3 well has been opened frequently as a demonstration, and the well pressure has remained constant or slightly increased. A 24-hour "flow test" in 2011 was conducted to 'cook a pig' (BBQ) for the 2011 Southeastern Section meeting, Geological Society of America field trip lunch (Reid and others, 2011). During that event, the well pressure for the shale interval (5.5-inch pipe) began with a well pressure of 1,100 psi. After a day of cooking a pig (stepped down gas pressure but frequent free venting of the well for interested on-lookers), the pressure was 900 psi.
The gas provided good steady cooking flame and sufficient BTU to cook the pig. The coal bed methane part of the well's pressure remained steady at ~212 psi before and after cooking the pig.

Notes (continued):

Simpson #1 - According to the mud log, the contact between the Sanford Fm. and the Cumnock Fm. is at about 2,292 feet. Three intervals in the Sanford Fm. have either a petroleum ordor, some yellow petroleum cut, or in one case, an estimated flow rate of 3,000 MCFD that diminished to 231 MCFD after three hours. Two intervals in the Cumnock Fm. had gas shows, and two more a yellow- or fair yellow cut. The contact between the Cumnock Fm. and the stratigraphically lower Pekin Fm. is at about 3,000 feet. This well's initial flow rate was 3,000 MCFD.

Elizabeth K. Gregson #1 - Drilled into the basin margin alluvial fan, this well encountered gas saturations in sidewall cores from gas that migrated from the basin center. Twenty-five equally-spaced sidewall cores were obtained between a vertical depth of 2,570.5 feet and 2,597.3 feet. Of these, gas saturation was reported for 21 samples. The mean gas saturation was 66.48%, and the standard deviation was 20.12. Twenty-five samples had reported a mean porosity of 2.80% with a standard deviation of 1.68 (data from NCGS well files).

The basin margin alluvial fan strata may be a potential reservoir of a continuous accumulation; potential seals are shale beds and / or faults.



(**Above**) Full composite well logs of the Butler #3 well (far left), and the Simpson #1 well (middle and right columns). The middle column is the upper part of the Simpson #1 well, the right column is the lower part of the Simpson #1 well. Perforation locations are shown by red dots.

Well logs courtesy of Ronald D. Perkins.

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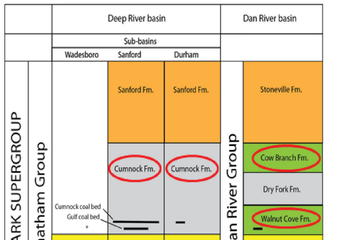


Stratigraphy for the Deep River and Dan River basins; this is slightly different than that used by Milici and others, 2012. The lacustrine strata are colored gray in the Deep River basin part of the figure, and colored green for the Dan River basin portion of the figure. The Cumnock Formation (Deep River basin) and the Cow Branch and Walnut Cove formations (Dan River basin) are the organic source rocks and unconventional reservoirs; the red ovals identify these formations. The Deep River basin stratigraphy is from Reinemund (1955), and the stratigraphy for the Dan River basin is from Olsen and others (2015). The Cumnock Fm. and Walnut Cove Fm. are interpreted as early Norian Age (225-227 Ma); the Cow Branch Fm. is late-early to middle Norian Age (217-222 Ma) (Olsen and others, 2014).

Well sampling methods

Overview

The Butler #3 and Simpson #1 wells were sampled 9 November 2014 to obtain data for comprehensive molecular and stable isotope analyses of the noble- and hydrocarbon components (including liquids if present). The noble gases of interest are helium (He), neon (Ne), argon (Ar), and xenon (Xe).

Samples were collected using virgin Swaglok pressure vessels. Two samples were collected at each well. Previously molecular compositions and stable isotope data were collected in 2009 from both wells. The wells were thoroughly flushed (not done in 2009) to obtain comparison samples. A strong and permeating light hydrocarbon odor was present when both wells were flowed. A white cone of white vapor surrounded by a clear and colorless gas in the Butler #3 gas stream is thought to be condensate when the well was flowed.

Butler #3 well (Samples Butler 3A and 3B)

The well pressure was 850 psi before flushing. Previously, this well was "flow tested" for 24 hours using a series of step down valves to literally cook a pig for a regional geology meeting during which the pressure remained constant.

To flush the well bore, it was flowed at ~1/8" open for two minutes after which the pressure was 825psi. The well was rested for several minutes to allow pressure recovery. The well valve opening of ~1/8th was held constant through four well bore flushes. The well bore flushing was again for two minutes. The pressure at the start of the 2nd flow was ~840 psi and at the end it was was 825 psi. The well was rested for ten minutes after which the pressure was 825 psi. During both well flushings, the well began to "throttle" after about 1.5 minutes; we interpret this as possibly gas moving through liquid hydrocarbons and/or water.

The third flushing was after a ten-minute rest and the pressure was 825 psi. After two minutes the pressure was 790 psi. Pressure recovery began immediately and after five minutes the pressure was ~805 psi.

The fourth flushing was for two minutes during which the well sounded like it "slowed down" after one minute; the ending pressure was 790 psi.

Sample collection began with the sample vessel, previously fitted to the well, was four times filled, closed, vented, and closed. This procedure was followed for duplicate sample canisters from each well. The Butler #3A canister had a filled pressure of 85 psi; the Butler #3B canister had a filled pressure of ~85 psi.The canisters were then shipped to the USGS laboratory in Denver, CO, for analysis.

Simpson #1 well (Samples Simpson 1-A and 1-B)

Similar sample collection procedures were followed for the Simpson #1 well. Initial pressure measure indicated a lower pressure (~185 psi) than when measured at ~250 psi in March 2009. This was attributed to slow leaks around the ball valves. There was a strong petroleum odor around the well head, and what appeared to be dried oil material on well fittings. The well was run briefly to check the safety of the ball valve; a strong petroleum odor was noted, much like the Butler #3 well.

A contingency sample (Simpson 1-A) was planned because of lower well head pressure, possible watering in of the well, or just lower pressure because of valve leakage. The well was flowed for 15 seconds after which the pressure was 90 psi. A strong petroleum odor lingered.

The Simpson 1-A sample was collected after the canister was attached to the well, and four flushes were done - each for 10 seconds to flush the sample canister for a total time of 40 seconds. After the fourth 10-second flush, the pressure was 88 psi and a strong petroleum odor remained. For this sample, the well was open about ¼ and pressure was measured on a ½-inch cleaned stainless steel pipe. The Simpson 1-A sample was collected in the same manner as that of the Butler #3 well.

Prior to collecting the Simpson 1-B sample, the well was about opened to the 1/8th position, and flushed for one minute, closed briefly, and flowed because it was open for an additional minute to flush the well. The well was also flowed through a ½-inch stainless steel cleaned pipe. After the first minute, the starting pressure of 88 psi dropped to ~75 psi, and immediately recovered to 88 psi after resting the well. After the second flush, the pressure quickly recovered to 91 psi.

For the Simpson 1-B sample, the well was run full open through a ½-inch stainless steel cleaned pipe for one minute at after which pressure dropped to 15 psi. The well quickly recovered in two minutes to 40 psi, and after 15 minutes, the pressure was ~185 psi. The Simpson 1-B sample was collected using the previously described methods.

Butler #3 well

Simpson #1 well

Noble gas results

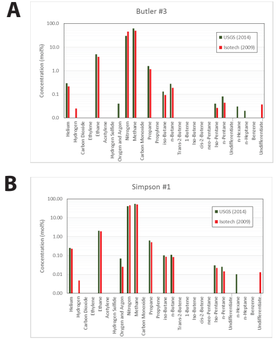
Sample	^{4}He ccSTP/cc ($x\ 10^{-6}$)	^{20}Ne ccSTP/cc ($x\ 10^{-9}$)	^{40}Ar ccSTP/cc ($x\ 10^{-6}$)	^{84}Kr ccSTP/cc ($x\ 10^{-9}$)	^{132}Xe ccSTP/cc ($x\ 10^{-9}$)										
Butler 3A	2363	0.108	33	1.43	0.041										
Butler 3B	2369	0.108	33	1.45	0.039										
Simpson 1-A	2015	0.044	54	1.83	0.049										
Simpson 1-B	2026	0.043	55	1.73	0.047										
Air	5.240	16.45	9308	650	23										
%err	1.0%	2.0%	2.0%	3.0%	3.0%										
Blank (Detection limit)	0.05	0.01	2	0.06	0.004										
	R R_A	$^{3}He/^{22}Ne$	$^{21}Ne/^{22}Ne$	$^{40}Ar/^{36}Ar$	$^{40}Ar/^{22}Ar$	$^{84}Kr/^{36}Kr$	$^{132}Xe/^{22}Xe$			$^{3}He/^{36}Ar$	$^{4}He/^{40}Ar^{*}$	$^{3}He/^{21}Ne^{*}$ ($x\ 10^{6}$)			
Butler 3A	0.074	9.760	0.0348	0.178	418.3	0.312	**			1.392	247.3	36.78			
Butler 3B	0.077	9.754	0.0342	0.178	417.5	0.300	**			1.372	247.6	40.90			
Simpson 1-A	0.068	10.001	0.0544	0.178	522.2	0.250	**			0.430	86.3	17.94			
Simpson 1-B	0.068	9.844	0.0493	0.177	524.6	0.283	**			0.413	84.8	22.78			
Air	1.000	9.800	0.02900	0.188	295.5	0.305	0.151			0.522					
Lab Err +/-	0.005	0.100	0.00030	0.005	5.0	0.015	0.010			0.280	8.00	22.40			
%err	0.50%	1.02%	1.03%	2.66%	1.69%	4.91%	6.63%			AIR/ASW	Radiogenic production				
	^{36}Ar ccSTP/cc ($x\ 10^{-6}$)	$^{3He}/^{36Ne}$ (xair)	$F^{4}He$	+/-	$F^{20}Ne$	+/-	$F^{84}Kr$	+/-	$F^{132}Xe$	+/-					
Butler 3A	0.078	68255	181986	4069	2.656	0.075	0.888	0.032	0.709	0.026					
Butler 3B	0.078	68839	180957	4046	2.619	0.074	0.890	0.032	0.660	0.024					
Simpson 1-A	0.103	142392	117215	2621	0.820	0.023	0.860	0.031	0.637	0.023					
Simpson 1-B	0.104	147270	116429	2603	0.788	0.022	0.801	0.029	0.606	0.022					
Air	31.5	1.0	1.000	0.022	1.000	0.028	1.000	0.036	1.000	0.036					
ASW		1.0	0.256		0.305		1.830		3.275						
ASSW		1.0	0.267		0.314		1.813		3.213						

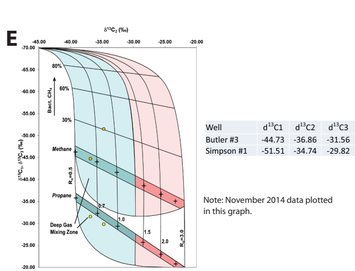
NOTES:

** 132Xe to low to measure

$FX = X/^{36}Ar_{samp} / X/^{36}Ar_{air}$

Molecular chemistry





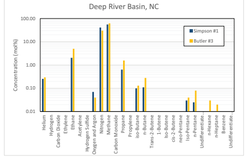
Well	$d^{13}C1$	$d^{13}C2$	$d^{13}C3$
Butler #3	-44.73	-36.86	-31.56
Simpson #1	-51.51	-34.74	-29.82

Note: November 2014 data plotted in this graph.

Note: November 2014 data plotted for graphs C, D.

Comparative table and graph of 2009 gas analyses *vs.* 2014 gas analyses for the Butler #3 and Simpson #1 wells

	Butler #3				Simpson #1			
	USGS (2014)		Isotech (2009)		USGS (2014)		Isotech (2009)	
Component	mol %	std dev	mol %	std dev	mol %	std dev	mol %	std dev
Helium	0.295	0.007	0.218	-	0.255	0.007	0.223	-
Hydrogen	nd	nd	0.025	-	nd	nd	0.0047	-
Carbon Dioxide	nd	nd	nd	-	nd	nd	nd	-
Ethylene	nd	nd	nd	-	nd	nd	nd	-
Ethane	5.030	0.000	3.86	-	2.045	0.007	1.89	-
Acetylene	nd	nd	-	-	nd	nd	-	-
Hydrogen Sulfide	nd	nd	-	-	nd	nd	-	-
Oxygen and Argon	0.040	0.000	nd	-	0.070	0.000	0.0251	-
Nitrogen	92.210	0.014	45.4	-	41.295	0.361	46.49	-
Methane	62.295	0.007	48.76	-	55.425	0.332	51.65	-
Carbon Monoxide	nd	nd	nd	-	nd	nd	nd	-
Propane	1.570	0.028	1.15	-	0.635	0.007	0.501	-
Propylene	nd	nd	-	-	nd	nd	-	-
Iso-Butane	0.130	0.000	0.093	-	0.100	0.000	0.0847	-
n-Butane	0.280	0.000	0.186	-	0.110	0.000	0.0814	-
Trans-2-Butene	nd	nd	-	-	nd	nd	-	-
1-Butene	nd	nd	-	-	nd	nd	-	-
Iso-Butene	nd	nd	-	-	nd	nd	-	-
cis-2-Butene	nd	nd	-	-	nd	nd	-	-
neo-Pentane	nd	nd	-	-	nd	nd	-	-
Iso-Pentane	0.060	0.000	0.0264	-	0.030	0.000	0.0216	-
n-Pentane	0.080	0.000	0.0436	-	0.025	0.007	0.0142	-
Undifferentiated C5	nd	nd	-	-	nd	nd	-	-
n-Hexane	0.030	0.000	-	-	0.010	0.000	-	-
n-Heptane	0.020	na	-	-	nd	nd	-	-
Benzene	nd	nd	-	-	nd	nd	-	-
Undifferentiated C6+	nd	nd	0.0366	-	nd	nd	0.013	-



Nitrogen content of the gas

Nitrogen comprised nearly half of the natural gas composition from the Simpson #1, and Butler #3 wells. However, the Dummitt-Palmer #1 well, a coal bed methane well, was drilled at the basin margin where a diabase sill assimilated the lower part of the Cumnock Fm. and "blackband", resulting in nearly pure methane from the stimulated well. Based on the depleted (-3 per mil) ^{15}N from the Simpson #1 and Butler #3 wells, the nitrogen source is thought to be from the denitrification of the ammonium sulfate contained in the "blackband" – a unit rich in ammonia sulfate and phosphate and contains from 3.8 to 12.4 gallons of oil per ton (Reinemund, 1955). The "blackband" consists of beds of ferruginous, thick-bedded shale near the coal seams; the most extensive "blackband" bed, between the main bench and lower benches of the Cumnock coal bed, is generally only 18 inches thick. Reinemund interpreted the "blackband" as accumulations of carbon and iron-rich muds in the coal forming swamp at a time of restricted accumulation of plant material and described the "black-band" as an ammonium sulphate and calcium phosphate as well as other constituents. McGlue (2013, personal communication to J. Reid) analyzed by x-ray diffraction, a "blackband" sample from drill holes BDH-9 (see drill hole log in Reinemund, 1955, p. 148-149). This was a very oily rock that emitted a petroleum odor; its bulk mineralogy consisted of siderite (44.2%), fluoroapatite (20.3%), illite (8.6%), pyrite (4.3%), quartz (3.8%), chamosite (1.3%), calcite (1.2%), gypsum (1.0%), and others plus amorphous (15.4%). High ammonia (NH_4) concentrations were known to be associated with organic-matter-rich intervals ("blackband") above and below the coal beds in the Cumnock Formation. Krohn and others (1988) made ion chromatograph measurements that showed the highest concentration of mineral-bound ammonium was in illite-rich layers 200 feet stratigraphically above the blackband horizon and that the nitrogen may be bound inorganically throughout the stratigraphic interval of the Cumnock Formation rather than being concentrated in the "blackband" interval. However, the average ammonium content in these intervals is rather low, generally less than 0.1 weight percent. They note that the highest concentrations of ammonium occur in an interval roughly 200- to 328 feet above the blackband in the Dummitt-Palmer #1 (LE-QT-1-82) and North American Exploration, Inc. well NCCM-1 (CH-C-01-81) drill cores. Krohn and others were not able to determine a direct cause for the distribution but noted that illite would provide a mineralogical site favorable for substitution. Nitrogen distribution studies in illite clays in Germany indicated that nitrogen-rich gases formed during the final stages of gas generation after methanogenesis practically ceased ([Mingram] Plessen and others, 2005; Littke and Krooss, 2009; Krooss and others, 1995). Isolation of the "blackband" and illite-rich strata during well completion may increase the BTU content of the Cumnock Fm. gas and improve its overall quality.

Oil and "blackband"

Oil in the Sanford sub-basin occurs as: oil in fractures, blebs in coal mines, degraded oil in red sandstones of the overlying Sanford Formation, pyrobitumen, and oil-rich iron-rich shale ("blackband") (See Reinemund, 1949, 1955). This diversity indicates the Sanford sub-basin generated oil and temperatures reached the oil window. The kerogen conversion and maturity from multiple wells in the Sanford sub-basin indicates that the condensate-wet gas zone was reached. Some over-mature data points of dry gas reflect local diabase dike heating and locally higher maturation temperatures. Several quarts of oil were collected at a depth of 3,000 feet from the Butler #1 well soon after it was drilled. The down hole video-log shows oil was oozing from fractures in red sandstone. Acoustic and temperature logs run in this well indicate gas escaping by the temperature drop from adiabatic gas expansion, and the hissing sound of escaping gas. The oil when warmed in your hand flows quickly and has a fruit-like sweet smell like that of light machine oil. The bottom of the hole was bone dry with dust swirls; the drill hole video shows the orthogonal fracturing in the shale in the bottom part of the hole. A chromatogram of the oil was obtained. The oil might be classed as high paraffin-, low flow temperature oil because it needs to be warmed in your hand before flowing.

Molecular chemistry

1. In general, the geochemistry of the samples collected in 2014 is consistent with what was observed in the samples collected in 2009 (**A, B**). Both wells contain slightly lower concentrations of nitrogen in 2014 compared to 2009, and consequently contain slightly higher concentrations of hydrocarbons (due to normalization to 100 mol %). This may be the result of more thorough flushing of the wells in 2014 compared to 2009.
2. The molecular and stable isotopic composition of the gases is fairly typical of thermogenic natural gases (**C, D**). The gas wetness and carbon and hydrogen isotopic composition of methane suggest that this gas was generated in the oil window of thermal maturity. This is consistent with the measured thermal maturity of the Cumnock shale in the Sanford sub-basin (%Ro= 0.8 - 1.0).
3. The carbon isotopic composition of methane, ethane and propane (2014 data plotted) suggests that there is the potential for a small biogenic methane contribution in the Simpson #1 well (**E**). Specifically, the δ13C of the ethane and propane in the Simpson #1 well are enriched relative to the Butler #3 well; however, the methane in the Simpson #1 well is depleted relative to the Butler #3 well methane. The simplest explanation for this situation is that a small amount of significantly depleted methane from a biogenic source has mixed with a thermogenic gas in the Simpson well. It is not known if the methane was generated in the shale prior to drilling, or if it is an artifact of the drilling and completion process (and the fact that the well has been shut-in for 15+ years).
4. Due to the possibility that biogenic methanogenesis may have been induced in the Simpson #1 well, the geochemistry of the gas collected from the Butler #3 well may be more representative of Cumnock shale gas in other parts of the Deep River basin.

Related data

1. Pressure build-up data were collected from the Simpson #1 and Butler #3 wells between January 4, 1999 to September 6, 1999 (Holmes, 1998). For the Simpson #1 well the initial tubing pressure in the coal zones was 780 psi and the final pressure was 1,200 psi. The final pressure was achieved on March 29, 1999 and it remained at that level until the test was completed on September 6, 1999. For the Simpson #1 well the initial casing pressure in miscellaneous shales and sands was 340 psi and the final pressure was 680 psi. For the Butler #3 well, the initial tubing pressure in the coals and shales was 260 psi and the final pressure was 680 psi. For the Butler #3 well, the initial casing pressure was 800 psi and the final pressure was 1,080 psi. The final pressure was achieved on March 8, 1999 and it remained at that level until the test was completed on September 6, 1999, and
2. Chromatograms of old oil samples: a) V.R. Gross #1 well - Fulton (1987); b) a 1983 analysis of a degraded high paraffin oil from a depth of 3,000 feet in the Butler #1 well (plugged and abandoned). The gas from the Dummitt-Palmer #1 well was flared (burned) (personal communication to J. Reid from O.F. Patterson III, 2013).

References

Federal Helium Program, Frequently Asked Questions, viewed 23 October 2013 at URL http://www.blm.gov/nm/st/en/prog/energy/helium/federal_helium_program/federal_helium_program.html.

Fulton, Sara, M., October 27, 1987, Geochemical analysis for The Chevron #1 Groce well (sic), North Carolina, 32 document pages (PDF).

Hoffman, C.W., and Beutel, R.A., 1991, The Dummitt-Palmer #1 coal bed methane test well, Lee County, North Carolina: North Carolina Geological Survey Open-File Report 91-1, 11p.

Helium Stewardship Act of 2013, Public Law 113-40—Oct. 2, 2013, http://www.gpo.gov/fdsys/pkg/PLAW-113pub40/pdf/PLAW-113pub40.pdf, viewed 12 August 2015.

Holmes, Michael, 1998, Petrophysical Report, Simpson No. 1 and Butler No. 3 (sic wells), Sanford Field, Lee County, North Carolina, Prepared for Amvest Oil and Gas, Inc. by Digital Formation, Inc., Denver, Colorado (report located in North Carolina Geological Survey well files.

Krohn, M.D., Evans, John, and Robinson, Gilpin R., Jr., 1988, Mineral-bound ammonium in black shales of the Triassic Cumnock Formation, Deep River basin, North Carolina, *in* Froelich, Albert J., and Robinson, Gilpin R., Jr., editors, Studies of the Early Mesozoic basins of the Eastern United States: U.S. Geological Survey Bulletin 1776, pp. 86-98.

Kroos, B.M., Littke, R., Müller, B., Frielingsdorf, J., Schwochau, K., and Idiz, E.F., 1995, Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations: Chemical Geology, v. 126, pp. 291-318.

Milici, R.C., Coleman, J.L., Rowan, E.L., Cook, T.A., Charpentier, R.R., Kirschbaum, M.A., Klett, T.R., Pollastro, R.M., and Schenk, C.J., 2012, Assessment of undiscovered oil and gas resources of the East Coast Mesozoic basins of the Piedmont, Blue Ridge Thrust Belt, Atlantic Coastal Plain, and New England Provinces, 2011: U.S. Geological Survey Fact Sheet 2012–3075, 2 p.
(Also available at http://pubs.usgs.gov/fs/2012/3075/.)

Mingram [Plessen], B., Hoth, P., Lüders, V., and Harlov, D. E., 2005, The significance of fixed ammonium in Paleozoic sediments for the generation of nitrogen-rich natural gases in the North German basin: International Journal of Earth Sciences, 94, 5-6, 1010-1022.

Littke, Ralf, and Krooss, Bernhard M., 2009, Unconventional Paleozoic gas resources in the German part of the Central European basin: AAPG European Region Annual Conference: Paris-Malmaison, France, pp. 77-81, AAPG Search and Discovery article #80056.

Olsen, P.E., Kent, D.V., Whiteside, J.H., Reid, J.C., and Taylor, K.B., 2014, Chrono-stratigraphic context of the biotic assemblages of the Dan River-Danville and Deep River basins (Newark Supergrp, Virginia and North Carolina, USA: Southeastern Section annual meeting of the Geological Society of America, Abstracts with Programs, v. 46, No. 3, p. 20 and at URL https://gsa.confex.com/gsa/2014SE/webprogram/Paper237388.html

Olsen, P.E., Reid, J.C., Taylor, K.B., Whiteside, J.H., and Kent, D.V., 2015, Revised stratigraphy of the Late Triassic age strata of the Dan River basin (Virginia and North Carolina, USA) based on drill core and outcrop data: Southeastern Geology, v. 51, No. 1, p. 1-31.

Reid, J.C., and Milici, R.C., 2008, Hydrocarbon source rocks in the Deep River and Dan River Triassic basins, North Carolina: U.S. Geological Survey Open-File Report 2008-1108, 28p.

Reid, J.C., Taylor, K.B., and Cumberbatch, K.N.S., 2010, Digital compilation map Sanford sub-basin, Deep River basin, parts of Lee, Chatham and Moore counties, North Carolina (Seismic lines, drill hole locations, geologic units from Reinemund, 1955), hydrocarbon shows (gas, oil, asphaltic - or combination) and %Ro in wells - Areas within dotted line inferred extent of %Ro ≥ to 0.8).

Reid, J.C., and Taylor, K. B., with contributions by Olsen, P.E., and Patterson, III, O.F., 2011, "Natural Gas Potential of the Sanford sub-basin, Deep River basin, North Carolina." 57p., *in* Taylor, Kenneth B. and Jeffrey C. Reid, editors, "Field Trip Guidebook – 60th Annual Meeting," Southeastern Section, Geological Society of America, Wilmington, North Carolina, March 2011. Note: updated and revised version of this field trip guidebook was prepared for the 2011 annual meeting of the Eastern Section, AAPG and is available as AAPG Search and Discovery Article #10366 at URL http://www.searchanddiscovery.com/documents/2011/10366reid/ndx_reid.pdf.

Reinemund, J.A., 1949, Geology of the Deep River Coal Field, Chatham, Lee and Moore counties, North Carolina: U.S. Geological Survey, Preliminary Map (in two sheets).

Reinemund, J.A., 1955, Geology of the Deep River coal field, North Carolina: USGS Professional Paper 246, 159p.

Schruben, P.G., R.E. Arndt, and W.J. Bawiec, 1998, Geology of the conterminous United States at 1:2,500,000 scale - a digital representation of the 1974 P. B. King and H. M. Beikman map: USGS Data Series 11, 1 CD.

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Num	Well name	Well type	Analytical lab	Lab number	Sample name	Sample pressure	Sample date	Carbon monoxide	Hydrogen sulfide	Helium	Hydrogen	Argon	Oxygen	Nitrogen	Δ15N	Carbon dioxide	Methane	Δ13C	ΔD	Ethane	Δ13C	ΔD	GPM	Ethylene	Propane	Δ13C	ΔD	GPM	C4H10	C4H12	Iso-butane	Δ13C	GPM	N-butane	Δ13C	GPM	Iso-pentane	GPM	N-pentane	GPM	Hexanes+	GPM	BTU	Specific gravity	Comment
1	Dummitt-Palmer #1	CBM	U.S. Bureau of Mines		Cumnock coal		1981	nd			nd		0.40	2.40		0.24	96.95			0.24					nd				nd	nd													986.85		Hoffman and Buetel, 1991; other HC's - not detected
2	Dummitt-Palmer #1	CBM	U.S. Bureau of Mines		Gulf coal		1981	nd			nd		0.12	3.05		0.16	96.40			0.27					<2ppm				nd	nd													976.45		Hoffman and Buetel, 1991; other HC's - not detected
3	Dummitt-Palmer #1	CBM	U.S. Bureau of Mines		Black shale		1981	nd			nd		0.28	10.85		0.17	88.40			0.30					0.0003				<2ppm	nd													908.95		Hoffman and Buetel, 1991; other HC's - not detected
4	Butler #3	Oil / gas	Isotech	160349		~900	3/25/2009	nd	nd	0.218	0.0250	nd	nd	45.60	-3.32	nd	48.76	-45.1	-178.5	3.86	-38.8	-175.8		nd	1.15	-31.61	-121.3				0.093	-31.96		0.186	-31.25		0.0264		0.0436		0.366		605	0.778	
5	Butler #3	Oil / gas	Gas Analytical Services, Inc.	103166		250.00	3/16/2013						0.0083	27.4039		0.005	65.2753			5.2632			1.40		1.4906			0.41			0.1244		0.04	0.2411		0.08	0.0329	0.01	0.0603	0.02	0.095	0.04	813.7896	0.7178	Packed off interval in Cumnock coal bed; BTU dry (800.5499 - saturated)
6	Simpson #1	Oil / gas	Isotech	160348		~250	3/25/2009	nd	nd	0.223	0.0047	0.0074	0.0177	45.49	-3.23	nd	51.65	-51.4	-174.8	1.89	-34.60	-151.4		nd	0.501	-29.66	-120.6				0.0847	-27.90		0.0814	-28.85		0.0216		0.0142		0.013		577	0.759	
7	Simpson #1	Oil / gas	Gas Analytical Services, Inc.	103XXX		60	11/2/1998						0.01	29.603		0.176	70.074			0.117			0.03		0.02			0.01																	Lab number not legible; rig released 12/19/1998

Panel 2 - Noble gas chemistry, molecular gas composition and isotopes, and related data

TABLE OF LEGACY GAS CHEMISTRY DATA, CUMNOCK FM., SANFORD SUB-BASIN, DEEP RIVER BASIN