Appendix L

Baseline Sampling Program – Methods and Purpose

April 30, 2014

Lee Hinman, P.E.
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Dear Mr. Hinman,

Samples were collected from eight springs and one well in Huntington Valley, Nevada (Figure 1) for Noble Energy prior to exploration drilling and hydro-fracturing activities. The samples were analyzed for a suite of chemical, isotopic, and radiochemical parameters (Table 1) to establish their background concentrations. The analytical results available as of today are shown in Table 2. The Desert Research Institute's analysis suite includes a variety of analytes to evaluate potential impacts to local groundwater from hydro-fracturing of the target shale units.

The chemical parameters and constituents of water including pH, total dissolved solids (TDS), cations (Ca, Mg, Na, K, B, Ba, Li, Sr), and anions (alkalinity [HCO_3, CO_3], Cl, SO_4, NO_3, F, Br, SiO_2) will be used to chemically characterize groundwater. Water from the target shale units is likely to be very high in TDS and chemically different from local groundwater (e.g. Rowan et al. 2011, Engle et al. 2012). If shale water was to mix with local groundwater, changes in the chemical character of the local groundwater would be evident. Cation and anion samples are filtered through a 0.45 μm cartridge filter prior to collection so that the dissolved phases are measured. Cation samples are preserved with concentrated nitric acid.

Shale often has elevated, naturally-occurring, radioactivity from the presence of uranium and its daughter products. It is expected that the target shale units in the area have uranium and its daughter products because of the presence of these elements in the granitic source rock in the Ruby Mountains. The radioactivity analyses of gross alpha, gross beta, radium-226, and radium-228 will be used to identify mixing of target shale water with local groundwater. These analyses have been shown to be an effect tracer of shale water in the Marcellus Shale in Pennsylvania (e.g. Rowan et al. 2011, Engle et al. 2012). One sample bottle for gross alpha and gross beta is preserved with nitric acid and one sample bottle does not require any preservative. Samples for radium-226 and radium-228 are preserved with nitric acid.

The isotopic tracers δ^2H, $\delta^{18}O$, and $\delta^{13}C$ will be used to characterize groundwater. It is assumed that water from the target shale units will have substantially different isotopic signatures (e.g. Sharma et al., 2011, Engle et al. 2012) as compared to local groundwater because the target shale water was likely derived from precipitation that fell under different climatic conditions than

more recently recharged groundwater. $\delta^{13}C$ samples are filtered through a 0.45 μm cartridge filter prior to collection and are preserved with zinc chloride. $\delta^{2}H$ and $\delta^{18}O$ samples are collected in glass bottles with Polyseal cone lids.

Isotopic tracers of methane ($\delta^{13}C$, $\delta^{2}H$) will be used to identify whether any methane found is biogenic or thermogenic in origin. Two distinct processes produce hydrocarbon gas: biogenic and thermogenic degradation of organic matter. Biogenic gas is formed at shallow depths and low temperatures by anaerobic bacterial decomposition of sedimentary organic matter. Thermogenic gas is formed at deeper depths by either thermal cracking of sedimentary organic matter into hydrocarbon liquids and gas or thermal cracking of oil at high temperatures into gas. The occurrence of biogenic gas is unrelated to the processes that form oil. Each process produces a different isotopic signature of methane so the isotopic signatures can be used to identify whether the methane came from the deep target shale units or from the near surface (e.g. Jackson et al. 2013). $\delta^{13}C$ and $\delta^{2}H$ of methane samples are preserved with concentrated hydrochloric acid.

Atmospheric noble gas concentrations are used as groundwater tracers since their dissolved concentrations in water are dependent upon the temperature and pressure when gas exchange occurs. When precipitation recharges and becomes groundwater, it is isolated from the atmosphere and retains its noble gas concentration at the time of recharge and does not change as groundwater flows. One of the noble gases, helium, can increase in concentration as groundwater flows because it is also produced by radioactive decay of uranium and thorium in aquifer rocks and can also come from upward diffusion from the earth's mantle. The source of helium in groundwater can be evaluated by examining the ratio of helium-3 and helium-4 isotopes. Helium-4 is also a major component of thermogenic natural gas. The abundance of noble gases and the isotopic composition of helium will be used to distinguish between potential sources of natural gas and between different fluids including shallow groundwater and water from the target shale units (e.g. Jackson et al. 2013).

Sampling quality is of utmost importance for accurate dissolved noble gas measurements. Noble gases have low solubilities in water and even a very small bubble in the sample can provide enough of a gas phase for noble gases to partition into it, thereby stripping the water sample of dissolved noble gases. Collecting samples from springs is particularly problematic; samples have to be collected as close to the spring orifice as possible and there must be adequate flow from the spring orifice to minimize loss of noble gases from the spring water to the atmosphere prior to sample collection. In situations where there is insufficient flow from a spring, such as a diffuse seep with no clear orifice, or where springs and wells have been modified such that the configuration allows groundwater contact with the atmosphere before a sample can be collected, samples were not collected. Samples are collected in refrigerator-quality copper tubes that are closed with special-made metal pinch clamps.

A variety of chemicals may be used to hydro-fracture shale to increase the production of hydrocarbons (e.g. http://fracfocus.org/chemical-use/what-chemicals-are-used). Many of these chemicals are used in very low concentrations or breakdown quickly and may not be useful in identifying the presence of hydro-fracturing fluids in groundwater. Based upon the list of hydro-fracturing chemicals provided by Noble Energy in Table 1 in the Noble Energy/DRI/NDEP/NDOM memorandum of understanding, an analytical suite of chemicals was developed to identify the occurrence of hydro-fracturing chemicals in groundwater. The chemicals in the analytical suite include short-chained alcohols, glycerins, glycols, ammonium persulfate, and acrylonitrile. This suite of chemicals was selected considering that they might be used in sufficient quantities during hydro-fracturing to be detected in groundwater, or that they might produce breakdown products that are sufficiently long lived and in sufficient quantities to be detected in groundwater. Samples are collected in factory cleaned and baked amber glass bottles.

If you need any further information or explanation on sampling techniques, the analytical methods used, or the analytical results, please do not hesitate to contact me.

Sincerely,

Ronald L. Hershey, Ph.D.
Associate Research Hydrogeologist

Cc: Jim Thomas, Greg Pohll

References

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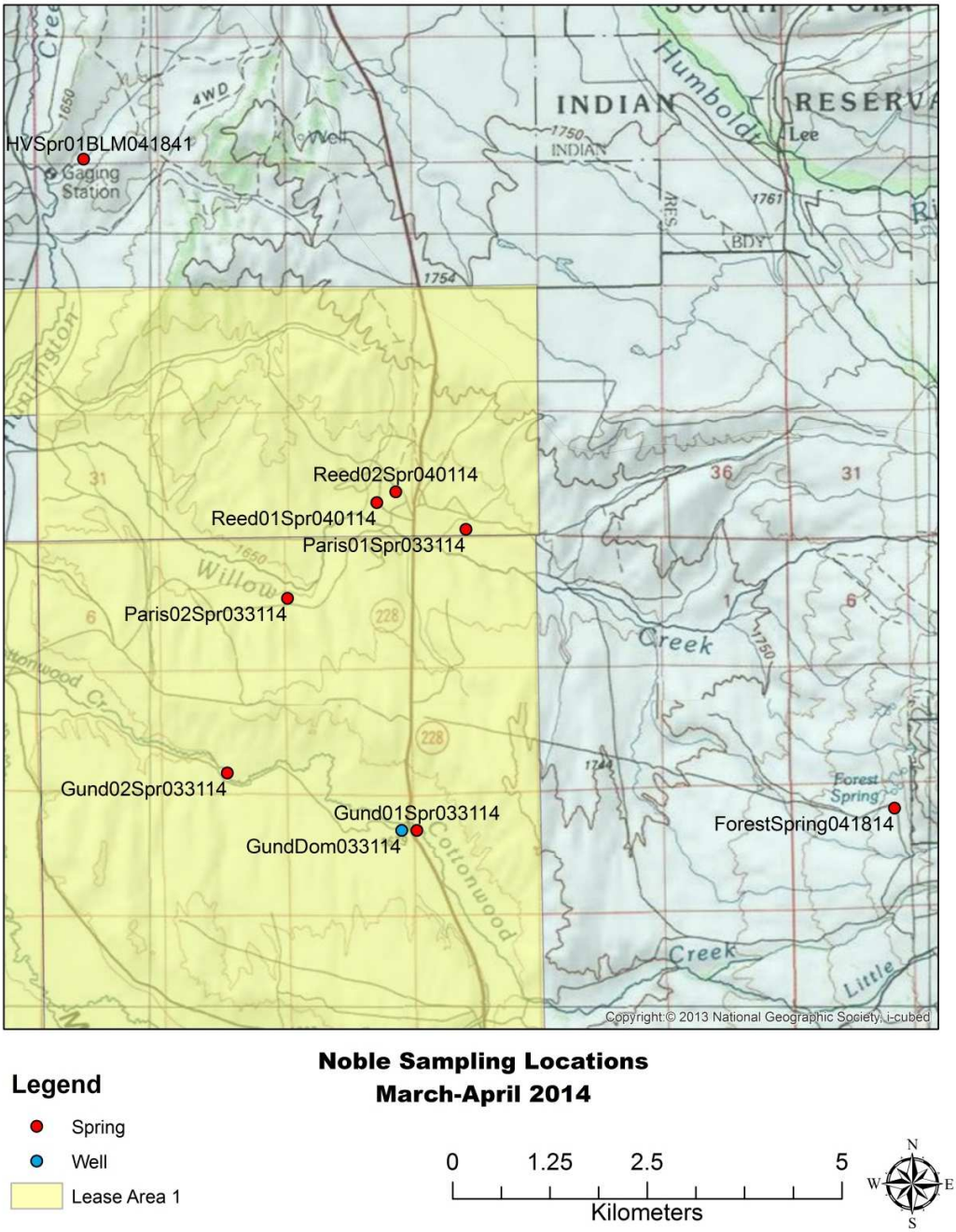

Figure 1. Groundwater sampling locations in Huntington Valley, Nevada.

Table 1. Chemical, Isotopic, and Radiochemical Parameters collected in Huntington Valley, Nevada.

Analyte	#	Bottle	Filtered Yes/No	Preservative	Notes
$\delta^{13}C$-CH_4	1	20 mL glass vial w/ septum	No	2 drops HCl	Add HCl before filling, no head space
$\delta^{2}H$-CH_4	1	20 mL glass vial w/ septum	No	2 drops HCl	Add HCl before filling, no head space
$\delta^{13}C$-DIC-water	1	20 mL glass vial w/ septum	Yes	$ZnCl_2$	Add $ZnCl_2$ before filling, no head space
$\delta^{2}H$, $\delta^{18}O$-water	2	40 mL glass w/ cone lid (send one; 2nd is duplicate)	No	None	Minimal head space, small bubble, 1 bottle is extra in case of breakage
Gross Alpha and Beta	1	500 mL plastic (provided)	No	2 mL HNO_3	HNO_3 already in bottle
Gross Alpha and Beta	1	125 mL plastic (provided)	No	None	
$^{226}Ra/^{228}Ra$	4	1 L plastic (provided)	No	4 mL HNO_3	HNO_3 already in bottle
Alcohols, glycerines, glycols, persulfate, acrylonitrile	2	125 mL amber glass	No	None	1 bottle is extra in case of breakage
Cations (Ca, Mg, Na, K, B, Ba, Li, Sr)	1	500 mL plastic	Yes	10 drops HNO_3	HNO_3 already in bottle
Anions (HCO_3, CO_3, Cl, SO_4, NO_3, F, Br, SiO_2)	1	500 mL plastic	Yes	None	
TDS	1	250 mL plastic	No	None	
Ne, He, $^{3}He/^{4}He$	2	copper tube & clamps	No	None	No bubbles

Table 2. Analytical Results for Groundwater Samples Collected in Huntington Valley, Nevada.

Location	Sample Date	$\delta^{13}C$ CH_4	$\delta^{2}H$ CH_4	$\delta^{13}C$ DIC Water	$\delta^{2}H$ Water	$\delta^{18}O$ Water	Gross Alpha	Gross Beta	^{226}Ra	^{228}Ra	Methanol	Ethanol	Isopropanol	Glycerol
Units		(‰)	(‰)	(‰)	(‰)	(‰)	(pCi/L)	(pCi/L)	(pCi/L)	(pCi/L)	(ng/µL)	(ng/µL)	(ng/µL)	(ng/µL)
Minimum Detection Limit							3	3	1	1	2.0	2.0	2.0	0.5
GundDom033114	3/31/2014	NA	NA	-12.80	-120.1	-15.28	NA	NA	NA	NA	ND	ND	ND	ND
Gund01Spr033114	3/31/2014	NA	NA	-14.91	-117.3	-15.28	TT	TT	NC	NC	ND	ND	ND	T
Gund02Spr033114	3/31/2014	NA	NA	-9.82	-117.0	-14.51	TT	TT	NC	NC	ND	ND	ND	ND
Paris01Spr033114	3/31/2014	NA	NA	-13.37	-123.9	-16.19	TT	TT	NC	NC	ND	ND	ND	ND
Paris02Spr033114	3/31/2014	NA	NA	-13.27	-126.0	-16.45	TT	TT	NC	NC	ND	ND	ND	ND
Reed01Spr040114	4/1/2014	NA	NA	-13.44	-121.6	-15.61	TT	TT	NC	NC	ND	ND	ND	ND
Reed02Spr040114	4/1/2014	NA	NA	-13.01	-119.4	-15.51	TT	TT	NC	NC	ND	ND	ND	ND
ForestSpring0418114	4/18/2014	-31.05	ND	-14.32	-127.9	-16.56	TT	TT	TT	TT	ND	ND	ND	T
HVSpr01BLM041814	4/18/2014	-18.24	ND	-10.22	-130.9	-16.67	TT	TT	TT	TT	ND	ND	ND	ND

NA = not available
NC = not collected
ND = none detected (below minimum detection limit)
T = possible trace amount detected, but below the minimum detection limit
TT = results to be reported by Tetra Tech from Test America

Table 2. Analytical Results for Groundwater Samples Collected in Huntington Valley, Nevada (continued).

Location	Sample Date	Ethylene glycol	Propylene glycol	2-Butoxyethanol	Acrylonitrile	Ammonium persulfate	Ca	Mg	Na	K	B	Ba	Li
Units		(ng/µL)	(ng/µL)	(ng/µL)	(ng/µL)	(ng/µL)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Minimum Detection Limit		0.5	0.5	0.5	2.0	1.0							
GundDom033114	3/31/2014	ND	T	ND	ND	T	NA	NA	NA	NA	NA	NA	NA
Gund01Spr033114	3/31/2014	ND	T	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
Gund02Spr033114	3/31/2014	ND	T	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
Paris01Spr033114	3/31/2014	ND	T	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
Paris02Spr033114	3/31/2014	ND	T	ND	ND	ND	TT	TT	TT	TT	TT	TT	TT
Reed01Spr040114	4/1/2014	ND	ND	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
Reed02Spr040114	4/1/2014	ND	T	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
ForestSpring0418114	4/18/2014	ND	ND	ND	ND	T	TT	TT	TT	TT	TT	TT	TT
HVSpr01BLM041814	4/18/2014	ND	ND	ND	ND	T	TT	TT	TT	TT	TT	TT	TT

NA = not available
NC = not collected
ND = none detected (below minimum detection limit)
T = possible trace amount detected, but below the minimum detection limit
TT = results to be reported by Tetra Tech from Test America

Table 2. Analytical Results for Groundwater Samples Collected in Huntington Valley, Nevada (continued).

Location Units Minimum Detection Limit	Sample Date	Sr (mg/L)	SiO_2 (mg/L)	HCO_3 (mg/L)	CO_3 (mg/L)	Cl (mg/L)	SO_4 (mg/L)	NO_3 (mg/L)	F (mg/L)	Br (mg/L)	TDS (mg/L)	Ne (cm^3STP/g)	He (cm^3STP/g)	$^3He/^4He$
GundDom033114	3/31/2014	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Gund01Spr033114	3/31/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NA	NA	NA
Gund02Spr033114	3/31/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NA	NA	NA
Paris01Spr033114	3/31/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NA	NA	NA
Paris02Spr033114	3/31/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NC	NC	NC
Reed01Spr040114	4/1/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NC	NC	NC
Reed02Spr040114	4/1/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NC	NC	NC
ForestSpring0418114	4/18/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NC	NC	NC
HVSpr01BLM041814	4/18/2014	TT	NC	TT	TT	TT	TT	NC	TT	TT	TT	NC	NC	NC

NA = not available
NC = not collected
ND = none detected (below minimum detection limit)
T = possible trace amount detected, but below the minimum detection limit
TT = results to be reported by Tetra Tech from Test America