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Summary and Preliminary Interpretation of Tritium and Dissolved Noble Gas Data from Site 300

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1 INTRODUCTION

In October 2013, groundwater samples were collected from 10 wells from Site 300 and analyzed by the Environmental Radiochemistry Laboratory at Lawrence Livermore National Laboratory (LLNL). Groundwater samples were analyzed for groundwater age tracers: tritium, the helium isotope ratio of dissolved helium and the concentrations of dissolved noble gases (Helium, Neon, Argon, Krypton, and Xenon). A subset of the samples was also analyzed for excess nitrogen due to saturated zone denitrification.

The age-dating data were used to evaluate the degree to which groundwater at a particular monitoring well was derived from pre-modern and/or modern sources. More specifically, the analyses can be used to determine whether the recharge age of the groundwater beneath the site pre-dates anthropogenic activities at the site.

2 ANALYTICAL METHODS

The Noble Gas Mass Spectrometer facility at LLNL has been operational for over ten years. The collection and analysis of samples is described in two SOPs (Visser et al., 2013a; Visser et al., 2013b). A groundwater sample for analysis of dissolved noble gases is collected by pumping water through a soft copper tubing (0.95 cm diameter, 35 cm length) that is subsequently sealed under back-pressure with steel pinch clamps to create a gas-tight cold weld. The cold-welded copper tube typically contains 9.75 grams of water, determined accurately by weighing tube and clamps before and after analysis. The helium isotope ratio and abundances of all noble gases (He, Ne, Ar, Kr, and Xe) are measured in groundwater samples in the laboratory by mass spectrometry techniques using a VG5400 noble gas mass spectrometer. The gas samples are prepared for mass spectrometric analysis using a combination of chemical gettering and cryogenic separations. Tritium concentrations were determined on 500 g sub-samples by the ^{3}He in-growth method (approximately 25 day accumulation time). Analytical uncertainties are approximately 1% for ^{3}He/^{4}He, 2% for He, Ne, and Ar, and 3% for Kr and Xe. Errors for derived parameters such as groundwater age and recharge temperature are propagated using analytical errors for the individual measured quantities.
From the concentrations of dissolved noble gases, recharge characteristics such as temperature and water table fluctuations can be derived. The accumulation of radiogenic helium-4 from the decay of naturally occurring uranium and thorium (U/Th) can be

interpreted as in indicator of groundwater residence times in the order of thousands of years. From the atom ratios of tritium and its decay-product helium-3, the groundwater residence time can be calculated for modern groundwater that has recharged since 1950. The combination of tritium and radiogenic helium-4 was used to classify a groundwater sample as fossil (>1000 years), pre-modern (recharged before 1950), modern (recharged after 1950) or mixed (evidence for both fossil and modern groundwater).

To detect excess dissolved nitrogen produced by denitrification, dissolved concentrations of N_2 and Ar were analyzed by Membrane Inlet Mass Spectrometry (MIMS) as described in Kana et al. (1994) and Singleton and Hudson (2005). The gas concentrations were calibrated using water equilibrated with air under known conditions of temperature, altitude, and humidity (25 °C, 183 m, and 100% relative humidity). Sample volume was 5 milliliters (mL), and each analysis took approximately 3 minutes. Samples were collected for MIMS analysis in 40 mL amber glass VOA vials, with no headspace.

Excess N_2 was calculated by subtracting the nitrogen present in the groundwater sample due to equilibration with the atmosphere and assimilation of excess air, similar to the method in Singleton et al. (2007).

Recharge temperature was determined based on dissolved Xe concentrations, and excess air was determined based on the concentration of Ne. Recharge elevation for each groundwater sample location was assumed to be at the surface elevation of the respective well.

3 RESULTS

10 samples were analyzed for tritium and 7 samples were analyzed for noble gases.

In six samples, tritium was not detected above the detection limit of 0.55 pCi/L (Figure 1). Four samples contained detectable amounts of tritium, containing at least a fraction of modern water. Two of those samples contained quantifiable concentrations of tritium, of 2.0±0.35 and 4.9±0.4 pCi/L. These concentrations are lower than typical present day concentrations of tritium in precipitation at the study site (~15 pCi/L).

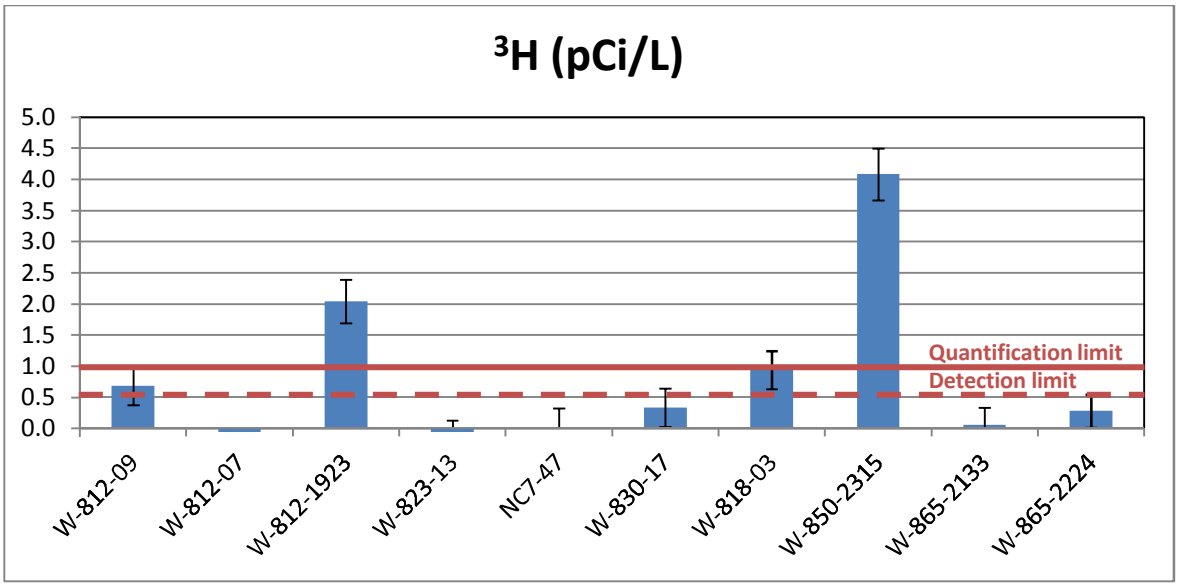

Figure 1: Tritium concentrations

For 6 of the 7 noble samples, a probability of an excess air model fit was obtained and derived noble gas parameters, such as recharge temperature, could be calculated. For two samples, the probability of the excess air model was less than 1%.

Recharge temperatures estimated from the noble gas concentrations vary between 17°C to 21°C, with a typical uncertainty of 1°C (Figure 2). The amount of excess air, expressed as relative excess to the equilibrium neon concentration at the recharge temperature (ΔNe), varied between 5% and 76%. These amounts of excess air indicate modest groundwater level fluctuations of less than 5 meters.

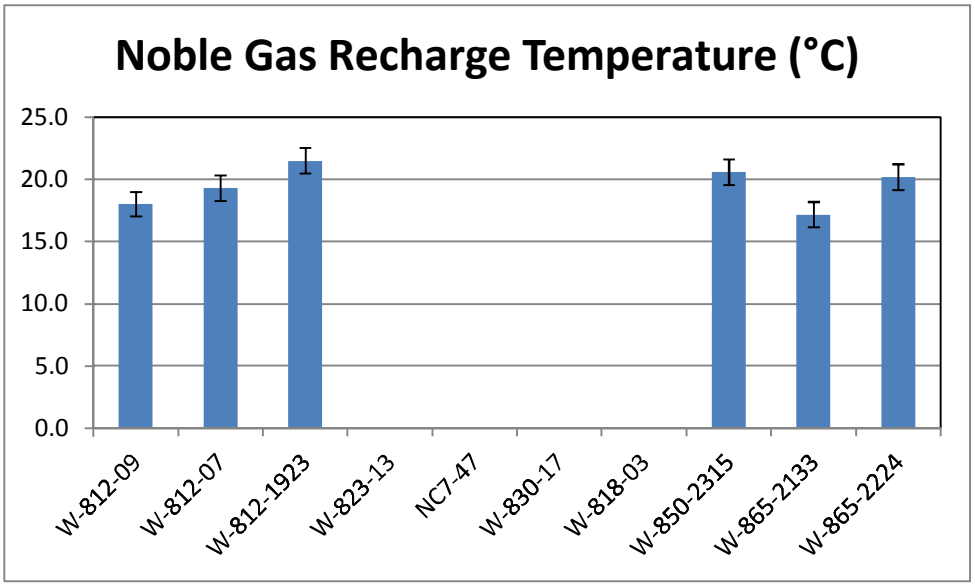

Figure 2: Noble Gas Recharge Temperature

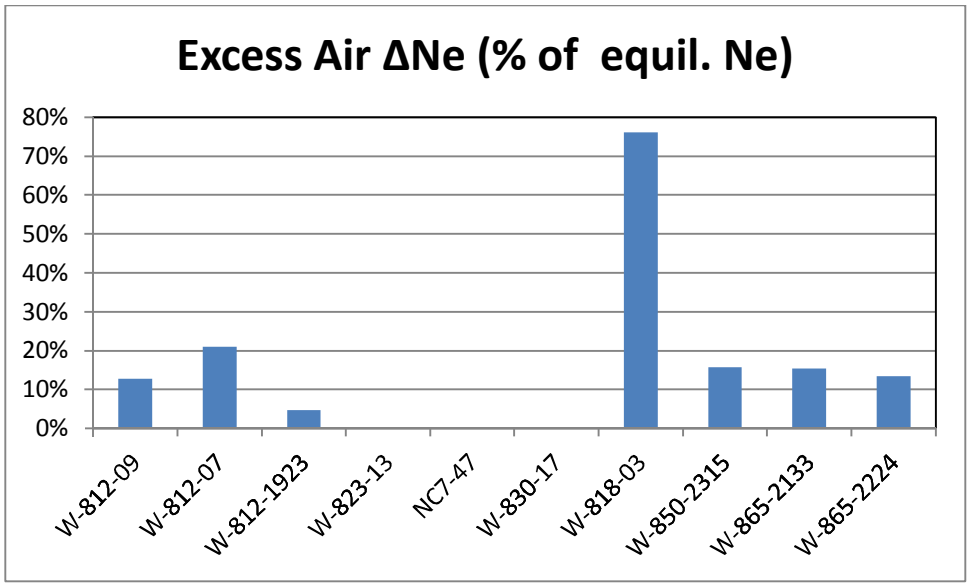

Figure 3: Excess Air

In one sample, a significant amount of terrigenic helium was detected (more than 3% of the equilibrium helium concentration at the recharge temperature). The helium isotope ratio of the terrigenic helium component indicated that the source was radiogenic, produced by U/Th decay. The amount of radiogenic helium-4, 10% of equilibrium helium, corresponds to a groundwater residence time of less than one thousand years, assuming typical crustal concentrations of U and Th.

Tritium-helium ($^3H/^3He$) groundwater ages were calculated for samples containing more than 1 pCi/L tritium. For two samples, groundwater ages, varying from 0-10 years, were calculated with an associated uncertainty of 9-10 years. The large uncertainties of the $^3H/^3He$ ages are due to the relatively low tritium concentrations, and the presence of radiogenic helium in a subset of the samples.

Qualitative age interpretation

Based on the combination of tritium and radiogenic helium, the groundwater residence times can be qualitatively interpreted and the groundwater age classified into one of four categories: “fossil”, “pre-modern”, “mixed” or “modern”. The requirements of each category and the number of samples in each category are in Table 1.

Table 1: Qualitative age interpretation of well and seep samples in four categories.

Category	Tritium (pCi/L)	Terrigenic helium (% of equil. He)	Number of samples
Fossil	< 1	> 100%	0
Pre-modern	< 1	< 100%	6
Mixed	≥ 1	> 3%	2
Modern	≥ 1	< 3%	2

Based on the combination of tritium and radiogenic helium, the groundwater residence times can be qualitatively interpreted. (A quantitative age can only be estimated made if the tritium concentration is above the quantification limit.) Six samples, in which no tritium was detected, are considered "pre-modern". Two samples, containing detectable concentrations of tritium below the quantification limit, are considered a mixture of pre-modern groundwater with a small fraction of modern groundwater ("mixed"). Two samples, containing tritium and no radiogenic helium, are considered "modern". Considering the low concentrations of tritium, the "modern" groundwater samples are likely to contain a fraction of pre-modern groundwater.

4 SUMMARY AND CONCLUSIONS

The results of the tritium, dissolved noble gas, and excess N_2 analyses can be summarized as follows:

- Groundwater residence times at Site 300 range from pre-modern (recharged before 1950) to very young (< 10 years).
- Tritium concentrations in samples are low (< 5 pCi/L) and below the detection limit (0.55 pCi/L) in 6 samples. Samples from two wells (W-812-1923 and W-850-2315) contained quantifiable levels of tritium. Samples from two wells (W-812-09 and W-818-03) contained detectable tritium that was not quantifiable.
- Recharge temperatures vary from 17°C to 21°C.
- Excess air in groundwater indicates modest (<5 m) water table fluctuations.
- $^{3}H/^{3}He$ ages vary from 0 to 10 years in two samples (W-812-1923 and W-850-2315).
- Groundwater residence times were classified based on tritium and radiogenic helium as "pre-modern" (n=6), "mixed" (n=2) and "modern" (n=2).
- No significant excess N_2 was detected in any of the groundwater samples.

Analysis results																
ID	**date**	**^{3}H**	**±**	**D.L.***	**^{3}He/^{4}He**	**±**	**^{4}He**	**±**	**Ne**	**±**	**Ar**	**±**	**Kr**	**±**	**Xe**	**±**
		(pCi/L)			(-)		(cm^{3}STP/g)		(cm^{3}STP/g)		(cm^{3}STP/g)		(cm^{3}STP/g)		(cm^{3}STP/g)	
					(× 10^{-6})	(× 10^{-8})	(× 10^{-8})	(× 10^{-9})	(× 10^{-7})	(× 10^{-9})	(× 10^{-4})	(× 10^{-6})	(× 10^{-8})	(× 10^{-9})	(× 10^{-8})	(× 10^{-10})
W-812-09	10/08/2013	0.69	0.31	0.55	1.36	1.35	5.04	1.01	2.07	4.14	3.14	6.28	6.75	2.03	0.99	2.98
W-812-07	10/08/2013	-0.43	0.37	0.55	1.34	1.33	5.48	1.10	2.22	4.45	3.33	6.67	6.93	2.08	0.97	2.91
W-812-1923	10/08/2013	2.04	0.35	0.55	1.37	1.72	4.76	0.95	1.92	3.85	3.09	6.18	6.93	2.08	0.89	2.76
W-823-13	10/02/2013	-0.15	0.29	0.55												
NC7-47	10/02/2013	0.01	0.32	0.55												
W-830-17	10/02/2013	0.34	0.31	0.55												
W-818-03	10/03/2013	0.94	0.30	0.55	1.35	1.34	7.21	1.44	3.28	6.55	4.38	8.75	8.41	2.52	1.09	3.27
W-850-2315	10/08/2013	4.09	0.42	0.52	1.35	1.71	4.89	0.98	2.10	4.20	3.21	6.43	6.77	2.03	0.91	2.85
W-865-2133	10/08/2013	0.06	0.28	0.52	1.28	1.62	5.28	1.06	2.11	4.23	3.35	6.71	7.16	2.15	1.02	3.18
W-865-2224	10/08/2013	0.28	0.27	0.52	1.17	1.48	5.52	1.10	2.08	4.16	3.32	6.65	7.10	2.13	0.93	2.90

* 95% confidence level (2 σ)

Derived parameters										
ID	**date**	**Probability of Fit**	**Noble gas Recharge Temperature**	±	**Excess air ΔNe**	**Radiogenic Helium**	**Radiogenic Helium Age**	**$^3H/^3He$ Age**	±	**Age Category**
		(%)	(°C)	(°C)	(% of equil. Ne)	(% of equil. He)	(ka)	(a)		
W-812-09	10/08/2013	1%	18.0	1.0	13%	0%	0.0	>50	0	mixed
W-812-07	10/08/2013	41%	19.3	1.0	21%	0%	0.0	>50	0	pre-modern
W-812-1923	10/08/2013	3%	21.5	1.0	5%	2%	0.0	10	10	modern
W-823-13	10/02/2013							>50	0	pre-modern
NC7-47	10/02/2013							>50	0	pre-modern
W-830-17	10/02/2013							>50	0	pre-modern
W-818-03	10/03/2013	0%	bad fit	na	76%	0%	0.0	>50	0	mixed
W-850-2315	10/08/2013	26%	20.6	1.0	16%	0%	0.0	0	9	modern
W-865-2133	10/08/2013	49%	17.2	1.0	15%	3%	0.0	>50	0	pre-modern
W-865-2224	10/08/2013	1%	20.2	1.0	14%	10%	0.1	>50	0	pre-modern

Excess nitrogen measurements and calculations.
N_2-excess = [$(N_2/Ar)_{meas}$ - $(N_2/Ar)_o$] Ar_{meas}

ID	Date	N_2	±	Ar	±	$(N_2/Ar)_{meas}$	±	$(N_2/Ar)_o$	±	N_2-excess	±	N_2-excess	±
		(cm^3STP/g)		(cm^3STP/g)		(cm^3STP/g)				(cm^3STP/g)		equivalent mg/L-NO_3	
		(× 10^{-2})		(× 10^{-4})									
W-812-09	10/08/2013	1.25	0.06	3.22	0.16	38.9	2.8	39.8	1.2	-0.03	0.10	-2	5
W-817-07	10/08/2013	1.39	0.07	3.46	0.17	40.2	2.8	41.0	1.3	-0.03	0.11	-1	6
W-812-1923	10/08/2013	1.30	0.06	3.42	0.17	38.0	2.7	39.0	1.3	-0.03	0.10	-2	6
W-823-13	10/02/2013												
NC7-47	10/02/2013												
W-830-17	10/02/2013												
W-818-03	10/03/2013	1.40	0.07	3.36	0.17	41.7	2.9	39.9	1.9	0.06	0.12	3	7
W-850-2315	10/08/2013	1.53	0.08	3.73	0.19	41.0	2.9	40.4	1.3	0.02	0.12	1	7
W-865-2133	10/08/2013	1.44	0.07	3.36	0.17	42.7	3.0	40.0	1.2	0.09	0.11	5	6
W-865-2224	10/08/2013	1.31	0.07	3.15	0.16	41.5	2.9	40.1	1.3	0.04	0.10	2	6

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