5UU02360

Results of Radiokrypton Analyses of Monitoring Wells
AEC-7R, H-12R, and SNL-16
Near the Waste Isolation Pilot Plant, New Mexico

Neil C. Sturchio
Department of Geological Sciences
University of Delaware

April 8, 2016

This report was prepared for
Sandia National Laboratories
under contract 1557037

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy.

INTRODUCTION

The results documented in this report represent an extension of earlier work supported by Sandia National Laboratories (SNL) to explore the use of ^{81}Kr as a natural tracer of groundwater travel time in the Culebra Dolomite overlying the WIPP (Waste Isolation Pilot Plant) site near Carlsbad, New Mexico. The Culebra Dolomite Member of the Permian Rustler Formation is believed to be the most likely path for radionuclides to reach the accessible environment from the repository horizon in the bedded salts of the underlying Salado Formation. This report summarizes the methods, results, and preliminary interpretation of the radiokrypton analyses obtained for Culebra groundwater samples collected during June, 2015 from three monitoring wells near the WIPP site.

METHODS

The wells sampled for radiokrypton analysis were AEC-7R, H-12R, and SNL-16. Sampling was performed during June 16-19, 2015 by a procedure involving gas extraction from pumped groundwater in the field, using a portable membrane extractor (Probst et al., 2007). The cylinders were filled to pressures of 2.2 to 2.8 bars. The sampling apparatus and sample gas cylinders were shipped to SNL's Carlsbad site in New Mexico. The sampling of monitoring wells was performed by Neil Sturchio and Gavin Phillips (University of Delaware), who were assisted on site by SNL personnel. The sampling procedure extracted dissolved gas from the groundwater at each well and transferred it into a 5-lb. aluminum cylinder. Gas cylinders were filled to a pressure between 2.2 and 2.8 bars. The filled cylinders were shipped to the laboratory of Dr. Reika Yokochi at the University of Chicago. Dr. Yokochi verified that the cylinders had not leaked by checking their pressures, then separated Kr from the bulk gas by the method of Yokochi et al. (2008). The purified Kr from each sample was transferred to a small container and brought to the Laboratory for Radiokrypton Dating at Argonne National Laboratory for measurement of atom ratios of $^{81}Kr/^{83}Kr$ and $^{85}Kr/^{83}Kr$ by laser-based ATTA (atom-trap trace analysis) methods as described by Jiang et al. (2012). The Kr analyses were completed during January 20-22, 2016.

RESULTS

The results of ATTA analyses of radiokrypton isotopes ^{81}Kr (half-life = 229,000 years) and ^{85}Kr (half-life 10.76 years) are given in Table 1. The measured $^{81}Kr/Kr$ ratios in Table 1 are reported relative to those in modern atmospheric Kr, [i.e., $(^{81}Kr/Kr)_{sample}/(^{81}Kr/Kr)_{atm}$]. The original data report as received from Argonne is attached as Appendix 1.

Table 1. Radiokrypton data for samples collected during 2015

Well ID	Date of collection	Date of analysis	^{85}Kr (dpm/cc)	^{81}Kr (sample/air)
AEC-7R	6/16/15	1/21/16	5.90 ± 0.34	0.58 ± 0.03
H-12R	6/18/15	1/20/16	7.21 ± 0.36	0.49 ± 0.02
SNL-16	6/19/15	1/22/16	2.16 ± 0.22	1.05 ± 0.05

^{85}Kr -- The ^{85}Kr results are reported in units of dpm/cc (decays per minute ^{85}Kr per cubic centimeter of Kr). Modern atmospheric air contains ^{85}Kr at a concentration of approximately 81.8 dpm/cc. Thus, the ^{85}Kr results for the WIPP samples from June 2015 (Table 1) indicate that contamination of the extracted gas by modern atmospheric Kr during sampling was small, ranging at most from 2.5 to 8.5 %, assuming no detectable ^{85}Kr was present in the formation water being sampled. The samples from wells AEC-7R and H-12R have higher amounts of modern atmospheric Kr, which is consistent with the longer times required for sampling these wells and small air leakage rates in the apparatus during sampling.

^{81}Kr -- The measured ^{81}Kr/Kr ratios in Table 1 are reported relative to those in modern atmospheric Kr [i.e., $(^{81}Kr/Kr)_{sample}/(^{81}Kr/Kr)_{atm}$] and range from 0.49 ± 0.02 to 1.05 ± 0.05. The two low-transmissivity wells sampled in June 2015, AEC-7R and H-12R, have low ^{81}Kr/Kr ratios, 0.58 ± 0.03 and 0.49 ± 0.02, respectively. These values are similar to the low ^{81}Kr/Kr ratios (0.50 ± 004 and 0.67 ± 0.05) measured previously in two other low-transmissivity wells (SNL-8 and SNL-14, respectively) as reported by Sturchio et al. (2014). The high-transmissivity well sampled in June 2015 (SNL-16), however, has a measured ^{81}Kr/Kr ratio indistinguishable from modern atmospheric Kr (1.05 ± 0.05).

DISCUSSION

The measured values of the ^{81}Kr isotopic abundances in the June 2015 samples from the low-transmissivity wells AEC-7R and H-12R are substantially lower than that of air, indicating long groundwater residence times. The first step in estimating a groundwater residence time is to make a correction for the modern atmospheric Kr component based on measured ^{85}Kr concentration, as described by Sturchio et al. (2014). In this discussion, we use the same notation and calculation procedures as defined by Sturchio et al. (2014). Before correcting the ^{81}Kr/Kr ratios, ^{85}Kr is adjusted for decay from time of sampling to time of measurement. Next, the fraction of modern atmospheric Kr (F_{atm}) is estimated from the ratio of the corrected ^{85}Kr concentration to the ^{85}Kr concentration in modern atmospheric Kr. We assume that the $^{85}Kr/Kr$ ratio in modern atmosphere of the northern hemisphere during 2015 was ~2.48×10^{-11} based on publically available information (Dubasov and Okunev, 2010; Momoshima et al., 2010; Schlosser et al., 2015). This value may have a relative uncertainty of about 3%. The fraction of "old" Kr that is intrinsic to the Culebra groundwater (F_{gw}) is then obtained simply as

$$F_{gw} = (1 - F_{atm}) \qquad (1)$$

Next, the $^{81}Kr/Kr$ ratio of the intrinsic Culebra groundwater Kr fraction (R_{gw}), after being corrected for the modern atmospheric Kr contribution acquired during sampling, is given by

$$R_{gw} = [(^{81}Kr/Kr)_{sample}/(^{81}Kr/Kr)_{atm} - F_{atm}] / F_{gw} \qquad (2)$$

The R_{gw} value can be used to calculate a ^{81}Kr model age (t_{model}), which represents the apparent mean residence time elapsed between recharge and sampling, using the radioactive decay equation

$$t_{model} = -1/\lambda \ \ln(^{81}R_{gw}) \qquad (3)$$

where λ is the decay constant of ^{81}Kr, 3.03×10^{-6} yr^{-1}. The apparent ^{81}Kr model ages for AEC-7R and H-12R are about 198,000 years and 269,000 years, respectively.

As shown by Sturchio et al. (2014), the ^{81}Kr model age for the sample from SNL-14 does not agree with the mean travel time obtained from particle-tracking results of the numerical flow model used for WIPP performance assessment. Assuming that the numerical flow model results are correct, then the ratio of the mean travel time predicted by the flow model (t_c) to that obtained from equation (3) (t) is given by

$$t_c/t = k/(k+k_{diff}) \qquad (4)$$

where k is the decay constant of ^{81}Kr and k_{diff} is defined as the diffusive loss constant defined in equation (7) of Sturchio et al. (2014). The ratio of t_c/t calculated for SNL-14 was 0.244. In that case, the ^{81}Kr model age was ~132,000 years and the mean travel-time predicted by the flow model was 32,100 years. If we assume that the same t_c/t factor (0.244) applies to the samples collected in AEC-7R and H-12R, we can calculate corrected mean residence times for these wells. The corrected times for AEC-7R and H-12R are ~48,000 years and ~66,000 years, respectively. Assumption of a constant t_c/t factor may introduce a larger, but unknown, error into the diffusion-corrected mean residence times. The diffusion correction is based on an assumption about the effective diffusivity in the aquitard rock surrounding the Culebra Dolomite, which was estimated by Sturchio et al. (2014). If our assumed effective diffusivity is too low, then the diffusion-corrected mean residence times should be considered as upper limits. If our assumed diffusivity is too high, then the diffusion-corrected mean residence times should be considered as lower limits.

The values of F_{atm}, F_{gw}, R_{gw}, and the ^{81}Kr model ages and diffusion-corrected mean residence times discussed above are summarized in Table 2, with propagated analytical errors, along with comparable results for the two samples reported by Sturchio et al. (2014). The diffusion-corrected mean residence times are shown on a map of the WIPP area in Figure 1.

Table 2. Calculated Kr fractions, with calculated ^{81}Kr model ages (t_{model}) and diffusion-corrected mean residence times (t_c) in units of 10^3 years.

Well ID	F_{atm}	F_{gw}	R_{gw}	t_{model}, 10^3 yr	t_c, 10^3 yr
AEC-7R	0.069 ± 0.004	0.931 ± 0.004	0.549 ± 0.034	$198\ ^{+22}/_{-20}$	**48 ± 5**
H-12R	0.065 ± 0.003	0.935 ± 0.003	0.455 ± 0.002	$269\ ^{+19}/_{-18}$	**66 ± 5**
SNL-16	0.025 ± 0.003	0.975 ± 0.03	1.05 ± 0.05	< 17 **	**< 17 ** **
SNL-8	0.203 ± 0.016	0.797± 0.016	0.37 ± 0.06	$326\ ^{+62}/_{-51}$	**79 ± 14**
SNL-14	0.0128 ± 0.0001	0.9872 ± 0.0001	0.67 ± 0.05	$132\ ^{+28}/_{-22}$	**31 ± 6**

** upper limit of diffusion-corrected mean residence time for SNL-16 based on two standard deviations of analytical error on R_{gw} value. For comparison, this calculation for one standard deviation gives a diffusion-corrected mean residence time of 0 years.

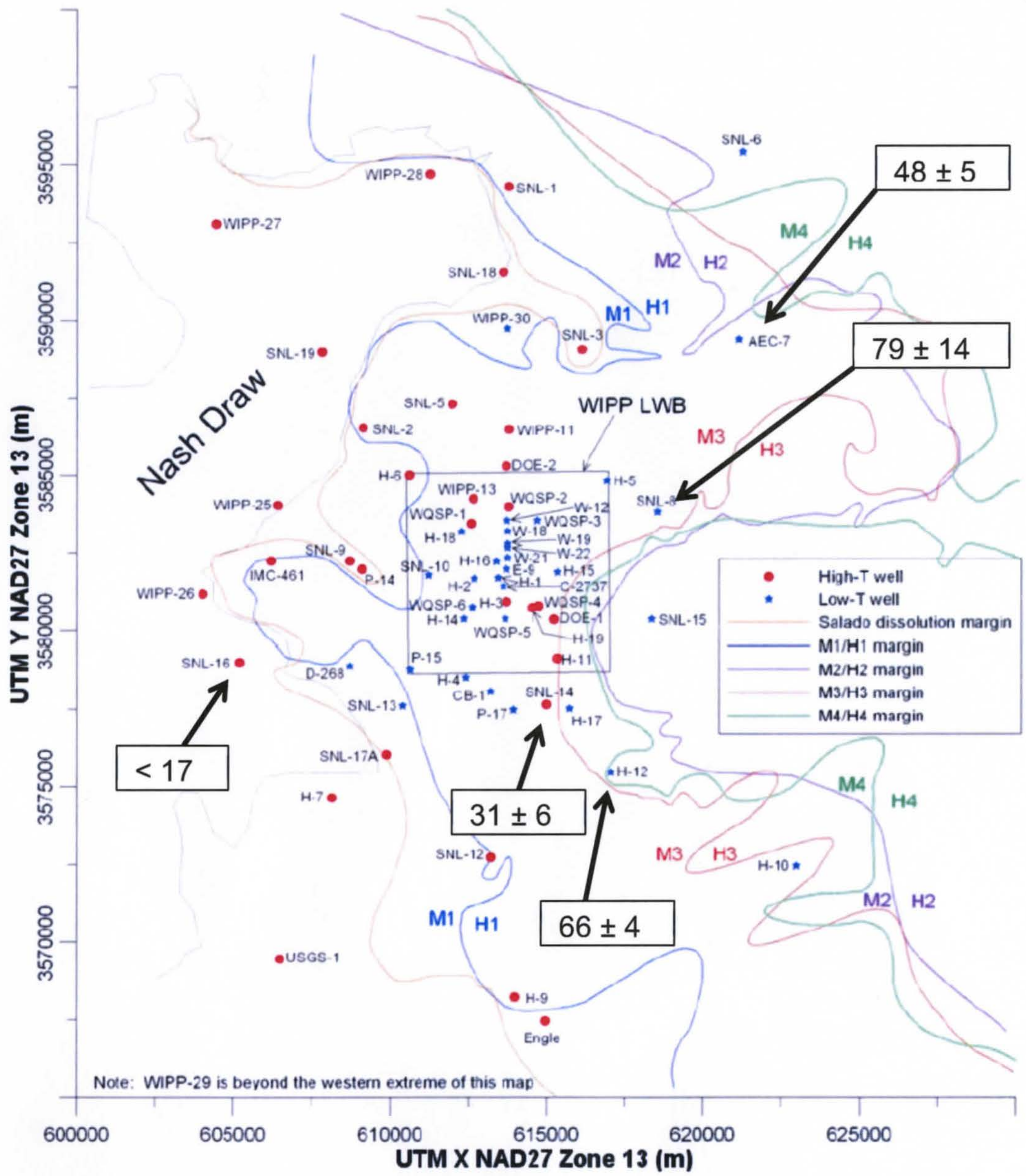

Figure 1. Map of WIPP area showing diffusion-corrected ^{81}Kr mean residence times from Table 2 (values in boxes, in units of 10^3 years) for Culebra Dolomite groundwater samples. Also shown are Rustler halite margins, Salado dissolution margin, single-well Culebra aquifer test locations, WIPP Land Withdrawal Boundary (LWB), and Nash Draw.

REFERENCES CITED

Dubasov Y.V. and Okunev N.S., 2010. Krypton and xenon radionuclides monitoring in the northwest region of Russia. *Pure and Applied Geophysics* 167, 487-498.

Jiang W., Bailey K., Lu Z.-T., Mueller P., O'Connor T.P., Cheng C.-F., Hu S.-M., Purtschert R., Sturchio N.C., Sun Y.R., Williams W.D., and Yang G.-M., 2012. ATTA-3: An atom counter for measuring ^{81}Kr and ^{85}Kr in environmental samples. Geochimica et Cosmochimica Acta 91, 1-6.

Momoshima N. *et al.*, 2010. An improved method for ^{85}Kr analysis by liquid scintillation counting and its application to atmospheric ^{85}Kr determination. *J. Environmental Radioactivity* 101, 615-621.

Probst P.C., Yokochi R., and Sturchio N.C., 2007. Method for extraction of dissolved gases from groundwater for radiokrypton analysis. In *Proceedings of the 4th Mini Conference on Noble Gases in the Hydrosphere and in Natural Gas Reservoirs*; GFZ Helmholtz Center: Potsdam, Germany, February 28-March 2, 2007. Accessed 29 February 2016 at: http://bib.gfz-potsdam.de/pub/minoga/minoga_probst-p-c.pdf

Schlosser C., Heidmann V., Konrad M., and Schmid S., 2015. Krypton-85 and radioxenon: Environmental tracers and indicators for nuclear activities. Paper presented at German Physical Society, Symposium on Applied Noble Gas Physics, Hedielberg, March 2015.

Sturchio NC, Kuhlman KL, Yokochi R, Probst PC, Jiang W, Lu Z-T, Mueller P, Yang G-M, 2014. Krypton-81 transport in the Culebra Dolomite aquifer near the Waste Isolation Pilot Plant, New Mexico. *Journal of Contaminant Hydrology* 160, 12-20.

Yokochi R., Heraty L.J., and Sturchio N.C., 2008. Method for purification of krypton from environmental samples for radiokrypton analysis. *Analytical Chemistry* 80, 8688–8693.

APPENDIX 1 – Radiokrypton Data Report for SNL Samples

Laboratory for Radiokrypton Dating, Physics Division, Argonne National Laboratory, Argonne, IL 60439
(630)252-4123 www.phy.anl.gov/mep/atta/

Atom Trap Trace Analysis (ATTA) Report

Report No. 034 **Report Date** 29 Jan 2016 **Project Name** WIPP

Samples supplied by: Neil Sturchio, Reika Yokochi (University of Delaware, University of Chicago)
Samples analyzed by: Jake Zappala, Peter Mueller (ANL)

ATTA trace No.	Sample No.	Sampling comments	Sampling Date	Sample Used (micro-L)	ATTA Date	^{85}Kr (dpm/cc)	^{81}Kr sample / air	ATTA Lab comments
10196	S8	H-12R	18 June 2015	~ 10	20 Jan 2016	5.50 ± 0.27	0.49 ± 0.02	$Kr : N_2 : O_2 : CH_4 = 1.0 : 2.3 : 0.2 : 1.1$
10197	S9	AEC-7R	16 June 2015	~ 10	21 Jan 2016	4.65 ± 0.26	0.58 ± 0.03	$Kr : N_2 : O_2 : CH_4 = 1.0 : 1.7 : 0.7 : 3.0$
10198	S6	SNL-16	19 June 2015	~ 10	22 Jan 2016	1.75 ± 0.18	1.05 ± 0.05	$Kr : N_2 : O_2 : CH_4 = 1.0 : 6.5 : 2.4 : 1.7$

Notes

- **^{85}Kr** ($t_{1/2} = 10.76 \pm 0.02$ yr) abundance is reported in the traditional unit of dpm/cc (decays per minute per cc STP of krypton).
  - Conversion: 100 dpm/cc corresponds to the isotopic abundance of ^{85}Kr/Kr = 3.03E-11.
  - The reported ^{85}Kr value is as measured on the ATTA analysis date. It may be significantly lower than the value on the sampling date due to radioactive decay in between the two dates.
- **^{81}Kr** ($t_{1/2} = 229 \pm 11$ kyr) abundance is reported as the sample-to-air ratio: $(^{81}Kr/Kr)_{sample} / (^{81}Kr/Kr)_{air}$.