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Abstract

Analysis of the relatively short-lived radionuclide sulfur-35 ($t_{1/2}$ = 87 days) provides useful insight into groundwater discharge from E-Tunnel at the Nevada National Security Site (NNSS). Discharge rates at E-Tunnel vary with precipitation, potentially as the result of short or fast flowpaths between recharge and discharge. The presence of sulfur-35 in groundwater would indicate a significant component of young (< 2-year-old) groundwater. We collected two large volume (20 L) samples of discharge water in November 2016. The samples were sent to Lawrence Livermore National Laboratory (LLNL), where they were processed and analyzed by Liquid Scintillation Counting (LSC). Sulfur-35 was not detected in either the sample or field duplicate, a finding consistent with E-Tunnel discharge containing no significant component of groundwater with age less than six months.

1. Background

From 1951 to 1992, the US government conducted 828 underground nuclear tests at the Nevada National Security Site (NNSS), about one-third of which occurred near or below the water table (US Department of Energy, 2015). Since the 1970s, the US Department of Energy (DOE) has been exploring the nature of radiologic groundwater contamination derived from these tests. Today, the Underground Test Area (UGTA) activity is characterizing the occurrence and movements of radionuclides in groundwater as derived from all underground tests conducted at the NNSS (Fig. 1). This work is proceeding through an integrated campaign of drilling and sampling, data interpretation, computer modeling, and broader monitoring activities, all conducted under a regulatory agreement between the State of Nevada, DOE, and the Department of Defense (NDEP et al., 1996, as amended).

Rainier Mesa (RM) is a relatively remote, topographically elevated volcanic formation in Area 12 of NNSS that served as a testing area for 61 underground nuclear tests (involving 62 distinct nuclear detonations) between 1957 and 1992 (USDOE, 2015). All but two of these were conducted within 10 horizontal tunnel systems mined into the face of the mesa, with the remaining two being conducted in vertical shafts constructed on its top (Fig. 2).

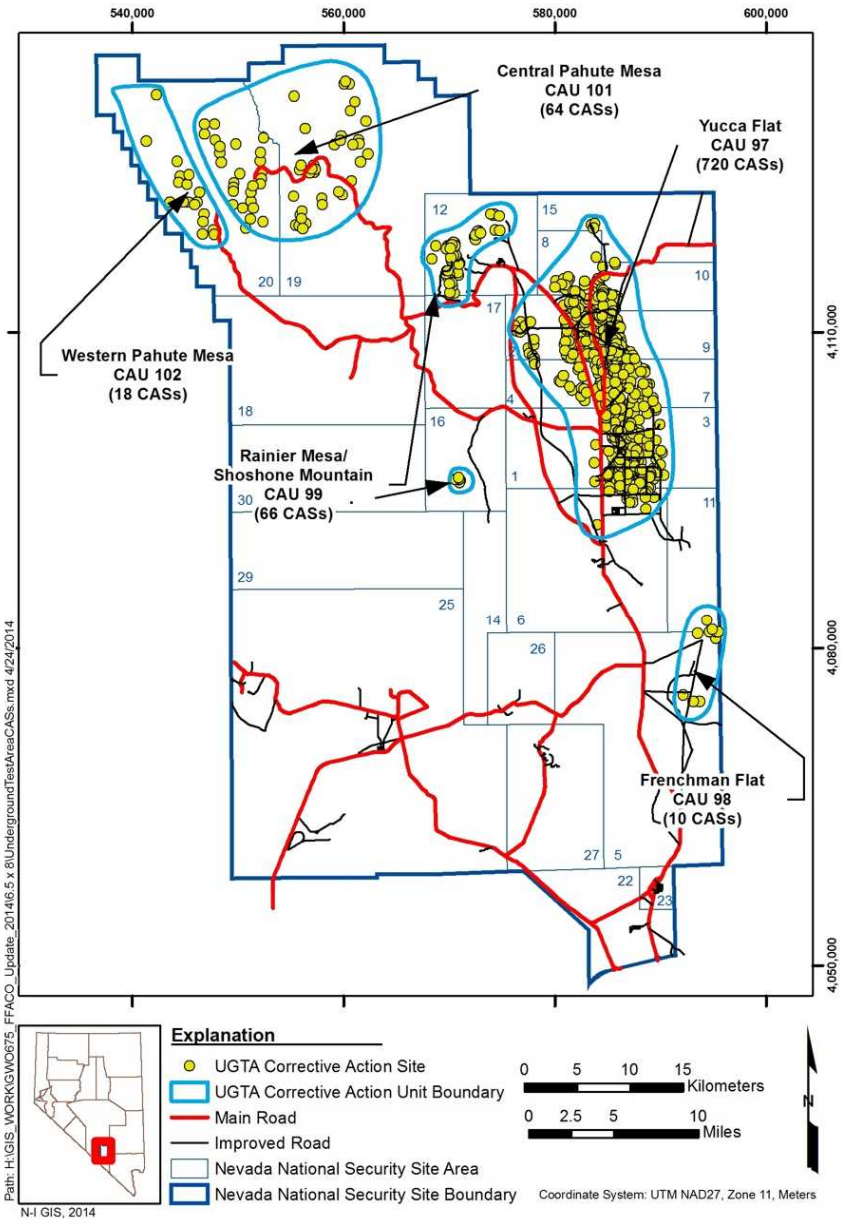

Figure 1: Map of the Nevada National Security Site showing the Corrective Action Sites associated with underground tests conducted between 1951 and 1992, after NDEP, et al., (1996, as amended). Rainier Mesa is located in Area 12.

The tunnel systems offered a unique environment for conducting the tests. Although they were all situated well above a regional carbonate aquifer, several were mined into a shallower volcanic aquifer that is perched, in places, above the deeper carbonate system. During incremental periods of tunnel construction, testing, and further tunnel expansion, perched groundwater was frequently intercepted, in some case continuously, and was channeled in drains towards the tunnel portals when the flows were persistent and significant. Specifically, in the E-, N-, and T-Tunnel systems, where such flows were prevalent, the discharges became increasingly

contaminated with radioactivity from the tests being conducted inside. This prompted the construction of three separate pond systems to capture and contain what became continuous radiologic discharges from the E-, N-, and T-Tunnel systems. Figure 3 shows a representative cross section through the E-Tunnel system showing the proximity of perched water to the tunnel drifts and testing locations, illustrating, conceptually, one of the mechanisms that contribute to observed discharges.

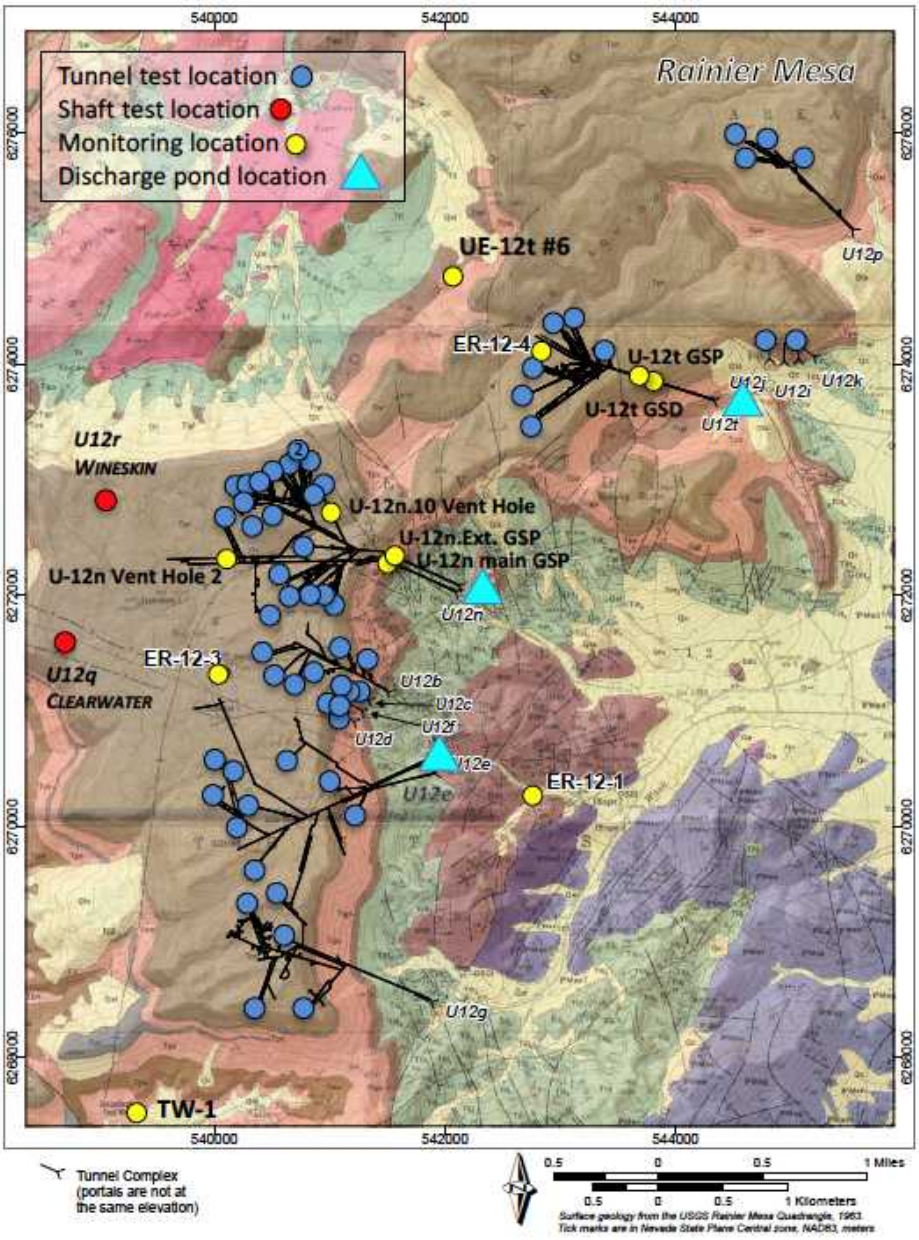

Figure 2: Map of the Rainier Mesa areas at the NNSS, showing the tunnel networks (lines), tunnel and shaft test locations (blue circles), nearby monitoring wells (yellow circles), and the E-, N-, and T-tunnel discharge ponds (lower, mid, and upper triangles at left, respectively).

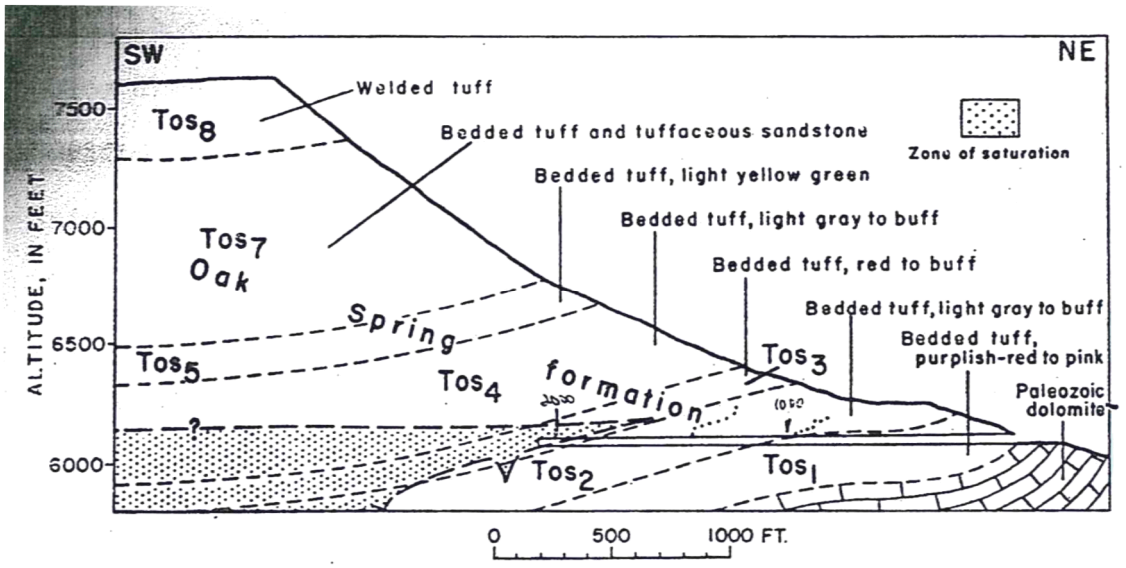

Figure 3: Representative cross section through the LOGAN – BLANCA drift in the E-Tunnel system showing the proximity of perched groundwater to the tunnel and testing locations within it (Clebsch, 1960).

Between 1992 and 1994, the N- and T-Tunnel portals were plugged, ending all of their surface water discharges and inducing the retention of all subsequent contaminated drainage within the tunnel drifts behind the plugs. The contaminated N- and T-Tunnel complexes are now completely flooded "reservoirs" extending back to all testing locations. A similar attempt to plug the E-Tunnel portal at that time was unsuccessful, so the E-Tunnel system continues to drain contaminated groundwater into the E-Tunnel ponds today (USDOE, 2017a).

Figure 4 shows a time series of contemporary E-Tunnel drainage flow rates and tritium concentration observed in the drainage between 1997 and April 2016 (Tompson, 2016)The drainage rates show a fairly regular series of small fluctuations occurring within each year, potentially attributable to seasonal precipitation or other variable groundwater effects in the tunnel complex. There are also a few more prominent, transient spikes in discharge that are irregularly spaced in time, which seem related to specific, high precipitation events, as shown in Figure 5.

The tunnel network will tend to aggregate water percolating into many different drifts and through many different testing centers into the observed portal drainage. Some portions of this water may have resided in the formation for long periods of time, while others may be relatively young enough to impart seasonal patterns or spikes the are correlated with specific precipitation events. It is plausible that inputs attributable to recent precipitation may occur (most likely) in the "shallower" portions of the network closest to the portal (Fig. 3) where the potential transmission times through the thinner mesa overburden are the smallest.

Interestingly, the fact that the decay-corrected tritium time series is fairly flat over the observation period suggest a fairly steady rate of contaminant input into the discharge during this period, although some "dilution" may be occurring around times of the high precipitation events.

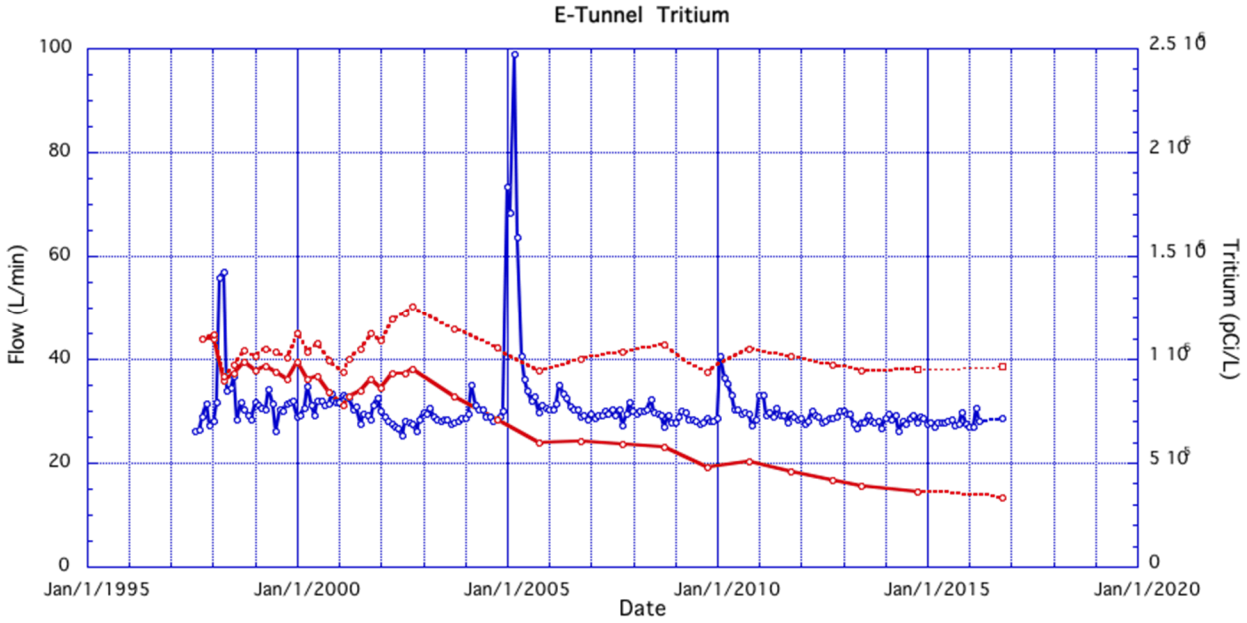

Figure 4: Time series of flow rate and tritium concentration (actual observed and corrected to 1997) in the E-Tunnel discharge between 1997 and October 2016. New flow and concentration data obtained on October 18, 2016 are highlighted.

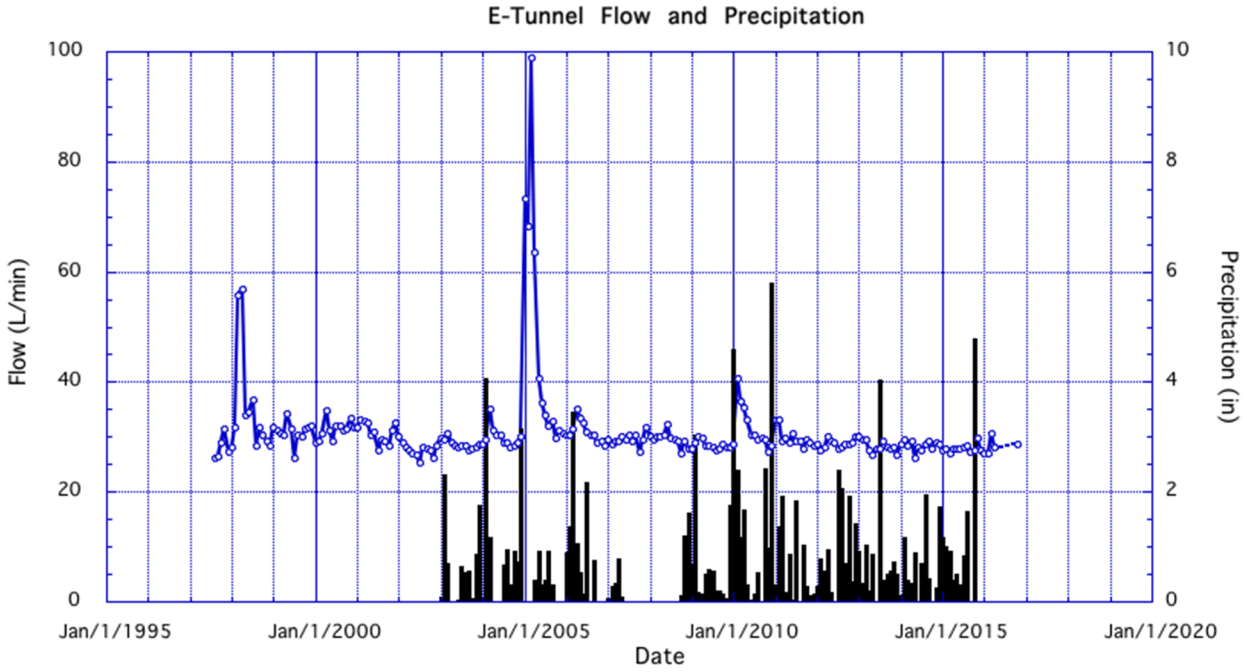

Figure 5: Time series of flow rate at E-Tunnel between mid-1997 and October 2016, along with measured monthly precipitation at Rainier Mesa. Precipitation data is incomplete over the time interval shown. New flow data obtained on October 18, 2016 are highlighted.

2. Objectives

The objectives of this report are to summarize an effort to assess the provenance of E-Tunnel discharge water – or a portion of it – using a sulfur-35 age dating technique. Sulfur-35 ($t_{1/2}$ = 87 days) is a cosmogenic radionuclide continually formed in the upper atmosphere and deposited at the earth's surface as sulfate, as wet or dry deposition. As such, this naturally occurring radioisotope is a useful intrinsic tracer for investigating the provenance of surface water and groundwater ages (and hence, their provenance and/or travel times) that are on the order of months to 1.5 years.

By seeking to identify the presence of sulfur-35 in the E-Tunnel discharge, the study would test the hypothesis that the discharge water contains a component of recent or very recent recharge received via direct percolation from the formation into one or more locations along the tunnel network.

The current study was based on a sampling event in October 2016, prior to the onset of winter season precipitation. The nominal fluctuations in the discharge rate are evident in the records of 2105 and early 2016 (Figs. 4, 5) despite several years of below-normal precipitation.

Lack of a positive sulfur-35 identification would indicate either that

- No part of the discharge (at this time of year) is younger than, six months in age, or
- Any such young portion that does exist is too small for the method to identify because of intrinsic detection limits

In this case, is also possible that a positive sulfur-35 identification could potentially found if sampling occurred during or after a period of extended rain (for example, at the end of the winter precipitation season), or if improved detection limits could be established.

3. Field Sampling & Analysis

3.1 Field Sampling

On October 18, 2016 at 07:30, staff members Sarah Roberts and Amanda Deinhart from Lawrence Livermore National Laboratory (LLNL) arrived at Building 310 on the NNSS to meet with UGTA personnel (from DOE and Navarro Research and Engineering) and to be briefed on sampling plans and logistics at E-Tunnel. Later, LLNL staff arrived at E-Tunnel at 09:30 to observe the sample collection activities. UGTA and Navarro staff set up a table with sampling supplies and equipment adjacent to the flume box through which the tunnel discharged was routed, and a sample of the water from the flume box was collected using a peristaltic pump. Altogether, UGTA staff collected twelve 4-L cubitaners of water to be returned to and analyzed at LLNL for sulfur-35. Six cubitaners of water (comprising a total of ~21 kg) were collected as a primary sample; and six additional cubitaners of water were collected as a field duplicate.

Navarro staff collected additional samples for other chemical measurements and also measured the flow rate (USDOE, 2017b). The flow rate was measured to be 28.68 L/min while subsequent analyses for tritium showed a concentration of 3.31E+05 pCi/L (Figs. 4 and 5).

3.2 Laboratory setup and liquid scintillation counting instrument calibration

Sample processing at LLNL took place in the low-level UGTA laboratory. Amanda Deinhart, the analyst, consulted with the lab managers, and with the assigned Environment, Safety and Health staff (including a Health Physicist) to ensure that all policies and procedures were in place to perform the work safely. Sample preparation, chemistry and analysis follow Uriostegui et al. (2015).

Prior to sample analysis, the liquid scintillation counter (LSC) was calibrated for background and efficiency with mock samples containing sulfate at levels expected to be present in actual samples. Sulfate concentration in E-Tunnel discharge has steadily remained at 16 mg/L for several years. Mock sulfate samples were created using a known amount of Na_2SO_4 to bracket the upper and lower limits of the E-Tunnel sulfate concentration (14 mg/L and 20 mg/L). For each concentration, two mock samples were created, one for LSC background determination and one for LSC efficiency. To calculate LSC background and quench parameters, un-spiked mock samples were counted on a Quantulus 1220 LSC for 450 minutes. To calculate LSC efficiency, mock samples were spiked with 835 dpm of sulfur-35 and counted for 450 minutes. The background for the samples on the LSC was determined to be 0.87 cpm with a 28% efficiency.

3.3 Sample radiochemistry and radioanalysis

Upon arrival at LLNL, samples were transferred from cubitaners via peristaltic pump into buckets lined with plastic bags. Each sample comprised 6 cubitaners of water, weighing approximately 21 kg. Samples were acidified with 5 M HCl until a pH of 3-4 was reached. The acidification process ensures that all sulfate is in solution. Additionally, 150 mg of Na_2SO_4 was added as a carrier to assist in the recovery of sulfate. Anion exchange resin (20 g of Amberlite IRA-400 chloride form) was added to the samples, which were then stirred for two hours with a spinner to keep the resin in suspension. Once the spinners were turned off, the resin settled to the bottom, water was decanted off and the remaining resin was transferred to a column. Sulfate was eluted from the anion exchange resin with 200 mL of 5% NaCl solution, which was collected in a beaker and acidified to a pH of 3-4 using 5M HCl. The samples were then heated on a hot plate and a barium solution ($BaCl_2 \cdot 2H_2O$) was added in excess to form a $BaSO_4$ precipitate. After two hours, the $BaSO_4$ precipitate settles out, is then decanted and transferred to a 50-mL centrifuge tube. The samples were centrifuged and rinsed with MQ water three times, and then transferred to a pre-weighed 20 mL glass scintillation vial and dried down in a drying oven at 100 °F overnight. Analyte precipitates were weighed after dry-down to obtain the mass of the $BaSO_4$ precipitate. The $BaSO_4$ precipitate was rehydrated with 5 mL of MQ water and then shaken to re-suspend the precipitate. A commercial scintillation cocktail (13 mL of Insta-Gel) was added to each vial, which was then shaken to evenly distribute the precipitate of the samples. The samples were then refrigerated for approximately 30 minutes to prep for liquid scintillation counting. After the samples were cooled, they were loaded onto the LSC and counted for 450 minutes each.

To correct for non-quantitative recovery of sample sulfate into the scintillation cocktail, a 5 mL aliquot was taken from each sample prior to the addition of any reagents. The sulfate in this aliquot was determined on the Metrohm 886 Ion Chromatograph and was compared to the mass of barium sulfate precipitate to calculate a chemical yield.

4. Results and Interpretation

4.1 Results

The sample and field duplicate contained 14-15 mg/L sulfate, consistent with previous analyses (albeit at the lower end of the range). **Sulfur-35 was not detected in the sample (UG100431) or in the field duplicate (UG100432)** – see Table 1 below. Reproducibility between sample and field duplicate was assessed by calculating the RER (the Relative Error Ratio calculated as ratio of the absolute difference in activity between two samples to the square root of the sum of the squared counting uncertainties for the two samples) – an RER of less than 3 is considered acceptable for radiochemical analysis of environmental samples. The calculated value of 0.98 for the sample and field duplicate in this study indicates that the sample and the field duplicate are not significantly different.

Table 1: Sulfur-35 analysis results

Sample ID	Sample Type	Collection Date	Count Date	Sample Sulfate (mg/L)	^{35}S Activity (mBq/L)	2σ Error (mBq/L)	MDA (mBq/L)
UG100431	E-Tunnel Discharge	10/18/16	3/14/16	15.024	0.66	1.48	1.76
UG100432	E-Tunnel Discharge	10/18/16	3/14/16	14.057	1.65	1.68	1.97

4.2 Interpretation

The non-detection of sulfur-35 in the sample and field duplicate indicates that E-Tunnel discharge on the date of collection did not contain a significant component of very young groundwater, i.e. that the times between recharge and discharge of all water sources in the tunnel contributing to the discharge was sufficiently long to allow sulfur-35 to decay to an undetectable level. To quantify this constraint requires some knowledge of the initial sulfur-35 activity in recharging water. No measurements have been made of sulfur-35 in NNSS rain or snow. Such measurements have been made in snow in the Rocky Mountains and in the Sierra Nevada. Snow in high elevation basins in the Rocky Mountains has 12 to 25 mBq/L sulfur-35 (Sueker et al., 1999; Michel et al., 2000; Michel et al., 2002). In a study of high-elevation basins in the Sierra Nevada, Uriostegui et al. (2016) estimated the fraction of new snowmelt in surface waters using data from snow collected over a hydrologic season and corrected for radioactive decay in the snowpack prior to snowmelt and recharge. Initial sulfur-35 in recharging snowmelt in the Sagehen Creek basin was estimated to be 7.4-8.3 mBq/L over two seasons. Mass-weighted full-column recharging snowmelt in the Martis Valley over one season was estimated to be 11.8 mBq/L. Using the Sierra Nevada estimates for initial sulfur-35 and assuming no mixing or dispersion in groundwater transport, the detection limits for sulfur-35 correspond to water

discharging from E-Tunnel having a groundwater age greater than 166 to 189 days. If mixing between old (>1.5 years) and young water occurs during transport, then the young water component may have a travel time of less than 166 to 189 days. For example, a mixture of ~50-70% old (>1.5 years old) and ~30-50% young (87-day-old) groundwater can also produce the observed results.

5. Conclusions and Summary

Water samples collected from the E-Tunnel discharge were determined to be below the minimum detectable activity for sulfur-35. Assuming bulk flow, non-detectable sulfur-35 indicates discharge of groundwater with an age in excess of six months. One limitation of the current study is that the detection limits are only about one quarter of the assumed initial sulfur-35, and only allow for detection of water younger than about two half-lives (approximately six months). For future analysis, collection and processing of larger volumes of water (e.g., 40-60 liters of water per sample) would allow better detection limits and stronger constraints on groundwater travel times. Measurements of the sulfur-35 composition in Rainier Mesa precipitation could also be developed to better constrain the detection limits. Collection of water at different times of the year (e.g., at the end of the rainy season) may also provide additional perspectives on the discharged groundwater age, especially with respect to the question of whether the small positive perturbations in discharge rate that occur after high precipitation events are produced by a contribution of recently recharge water to the water discharging from E-Tunnel. Moreover, it is also possible that an alternative, novel sodium-22 ($t_{1/2}$ = 2.6 yr) based analysis could be made as a means to detect young, but slightly older waters in the discharge (e.g., Sakaghchi, et al., 2005; Kaste et al., 2016).

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