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***Interpretation of stable isotope,
denitrification, and groundwater age data
for samples collected from Sandia National
Laboratories/New Mexico (SNL/NM) Burn
Site Groundwater Area of Concern***

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**Report to Sandia National Laboratories/New Mexico
(WFO Project D20024)**

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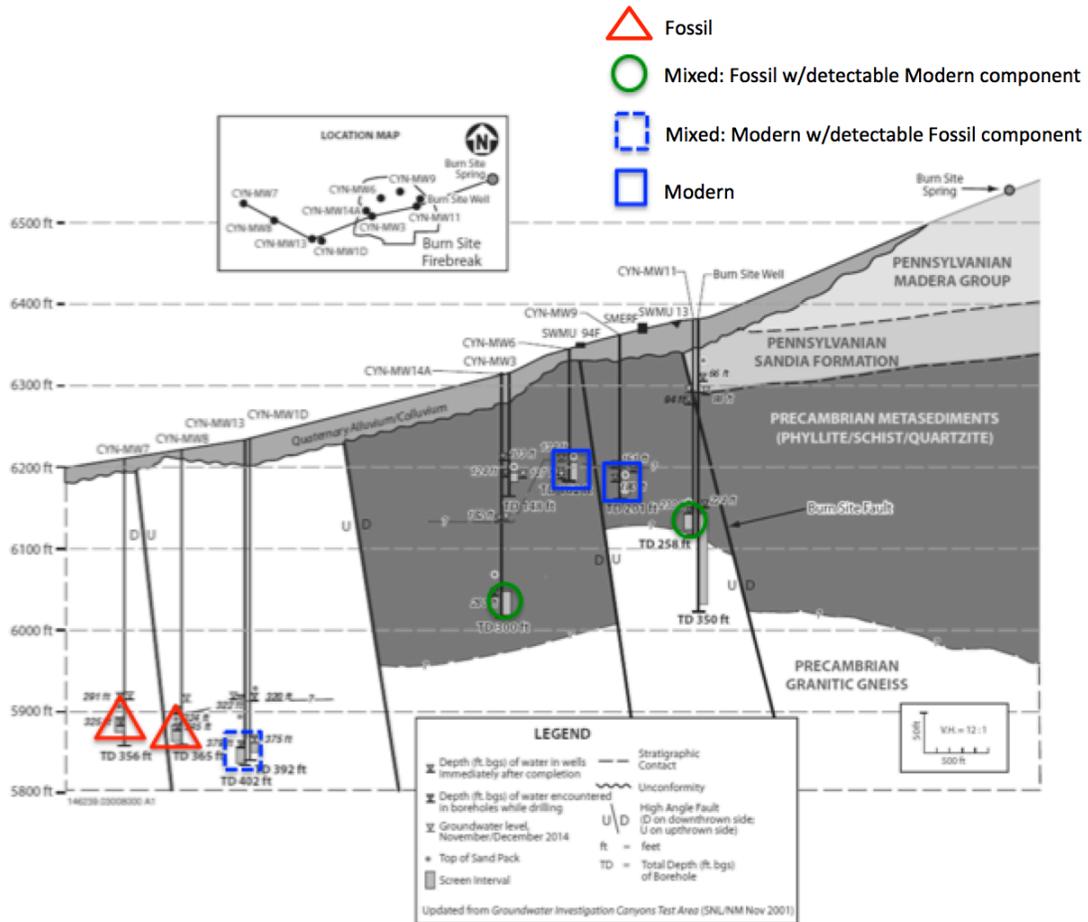
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Interpretation of stable isotope, denitrification, and groundwater age data for samples from the Sandia National Laboratories/New Mexico (SNL/NM) Burn Site Groundwater Area of Concern (LLNL-TR-694041)

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Prepared in cooperation with Sandia National Laboratory

1 INTRODUCTION

This report combines and summarizes results for two groundwater-sampling events (October 2012 and October/November 2015) from the Sandia National Laboratories/New Mexico (SNL/NM) Burn Site Groundwater (BSG) Area of Concern (AOC) located in the Lurance Canyon Arroyo southeast of Albuquerque, NM in the Manzanita Mountains. The first phase of groundwater sampling occurred in October 2012 including samples from 19 wells at three separate sites that were analyzed by the Environmental Radiochemistry Laboratory at Lawrence Livermore National Laboratory (LLNL, Madrid et al., 2013) as part of a nitrate Monitored Natural Attenuation (MNA) evaluation. The three sites (BSG, Technical Area-V, and Tijeras Arroyo) are shown on the regional hydrogeologic map (Figure 1) and described in the Sandia *Annual Groundwater Monitoring Report* (Jackson et al., 2011). The first phase of groundwater sampling included six monitoring wells at the Burn Site, eight monitoring wells at Technical Area-V, and five monitoring wells at Tijeras Arroyo. Each groundwater sample was analyzed using the two specialized analytical methods, age-dating and denitrification suites (Table 1). In September 2015, a second phase of groundwater sampling took place at the Burn Site including 10 wells sampled and analyzed by the same two analytical suites. Five of the six wells sampled in 2012 were resampled in 2015 (Figure 2).

Table 1. Constituents in the Age-Dating and Denitrification Suites

Age-Dating Suite	Denitrification Suite
<ul style="list-style-type: none"> • Tritium • $^3\text{He}/^4\text{He}$ • Noble gases (Helium, Neon, Argon, Krypton, and Xenon) 	<ul style="list-style-type: none"> • Stable isotopes of water: $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$ • Stable isotopes of nitrate in samples containing >1 mg/L-NO₃ nitrate: $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ • Dissolved nitrogen and argon gas concentrations • Total Organic Carbon

Groundwater age dating can be used to evaluate the degree to which groundwater at a particular monitoring well is derived from pre-modern and/or modern sources. More specifically, this analysis can be used to assess the timing and contribution of seasonal recharge to the groundwater beneath the BSG AOC relative to recent anthropogenic activities such as high explosives (HE) detonation and burning. Additionally, the data can be used to rule out the possibility that groundwater in some areas exhibits no evidence of recharge in modern times (i.e., during the last 50 years).

The analytical data from the denitrification suite can be used to evaluate the presence and magnitude of *in situ* nitrate reduction by detecting the presence of excess dissolved nitrogen gas

and any enrichment in the ^{15}N and ^{18}O of nitrate. Denitrification is a microbially facilitated process that reduces nitrate to molecular nitrogen (N_2) through a series of intermediate products. Denitrification typically occurs in oxygen-depleted, redox negative groundwater systems. If present, the degree of denitrification in groundwater is expected to increase along a groundwater flow path as the residual nitrate concentrations decrease with the isotopic composition, enriched in the heavier ^{15}N and ^{18}O isotopes and depleted in the ^{14}N and ^{16}O isotopes, relative to the original source nitrate. The ratio of the isotopic enrichment of nitrogen to oxygen is consistent across environmental settings, and has been empirically determined to be roughly 2:1 (Kendall, 1998). As a result of denitrification, the concentration of dissolved N_2 gas also increases.

Note that a key factor in any evaluation of natural attenuation of a natural inorganic constituent of groundwater such as nitrate, is an understanding of the: a) extent and magnitude of natural and anthropogenic nitrate source(s), b) aquifer recharge and discharge mechanisms, and 3) the continuity of groundwater flow pathways. As shown in the Burn Site Conceptual Hydrogeologic Model (Figure 3), the subsurface beneath the BSG AOC is complex due to variable bedrock stratigraphy and structure, and the presence of fractures and faults with unknown hydraulic connectivity. An understanding of the major processes that influence natural attenuation of nitrate in such a complex hydrogeologic setting requires the integration of several independent data sets (e.g., geochemistry, long-term spatial and temporal nitrate trends, hydraulic response under natural recharge and stress conditions, etc.) that are not part of this evaluation. In this report, LLNL summarizes results from two sampling events in order to evaluate evidence for *in situ* denitrification, the average age of the groundwater, and the extent of recent recharge of the bedrock fracture system beneath the BSG AOC.

2 ANALYTICAL METHODS

All analyses listed in Tables 1 and 2 were performed at Lawrence Livermore National Laboratory. Data quality objectives and reporting standards for the stable isotope analyses are summarized in Table 2. Stable isotopic analyses were determined using an IsoPrime gas source isotope ratio mass spectrometer (IRMS) in continuous flow mode. Molecules of interest are first converted to a simple gas prior to determining their stable isotope compositions. Oxygen isotope compositions in water are determined using an automated carbon dioxide equilibration method for $^{18}\text{O}/^{16}\text{O}$ based on the procedure of (Epstein and Mayeda, 1953). The hydrogen stable isotope compositions of water samples are determined by the high-temperature chromium reduction technique (Morrison et al., 2001). A small volume of water ($\sim 0.4\mu\text{L}$) is injected by an autosampler into an elemental analyzer containing chromium metal. The sample oxygen bonds with the chromium and the resulting H_2 gas is carried in a stream of helium to the IRMS.

Table 2: Data Quality Objectives and Reporting for Stable Isotope Analysis

Parameter	Method/ Range	Units	Reference	External Precision ¹	Instrumental Precision ²	
Nitrate Nitrate	$\delta^{18}\text{O}$ $\delta^{15}\text{N}$	Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{15}\text{N}$: Air $\delta^{18}\text{O}$: VSMOW	$\delta^{15}\text{N} \pm 0.3 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.8 \text{ ‰}$	$\delta^{15}\text{N} \pm 0.2 \text{ ‰}$ $\delta^{18}\text{O} \pm 0.5 \text{ ‰}$
Water Water	$\delta^{18}\text{O}$ $\delta^2\text{H}$	Dual Inlet and/or Continuous Flow Mass Spectrometry	Per mil (‰)	$\delta^{18}\text{O}$: VSMOW $\delta^2\text{H}$: VSMOW	$\delta^{18}\text{O} \pm 0.3 \text{ ‰}$ $\delta^2\text{H} \pm 2 \text{ ‰}$	$\pm 0.15 \text{ ‰}$ $\pm 1 \text{ ‰}$

1. External (1 sigma) precision objectives apply to replicate analyses of a single sample.
2. Instrumental precision (1 sigma) applies to calibration check samples, laboratory control samples and other measurements of samples of known concentration and isotopic composition where the known value is compared to the measured value.
3. VSMOW = Vienna Standard Mean Ocean Water.

Samples for isotopic analysis of nitrate ($\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$) were analyzed following a version of the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001; Singleton et al., 2005). In this method, a strain of denitrifying bacteria is used to reduce dissolved nitrate in water samples to N_2O gas that can be analyzed for N and O isotopic composition on the IRMS. The denitrifier method provides the results of the combined nitrate and nitrite signatures (Wankel et al., 2009).

In order to detect excess dissolved nitrogen produced by denitrification, dissolved concentrations of N_2 and Ar for this study were analyzed by Membrane Inlet Mass Spectrometry (MIMS) as described in (Kana et al., 1994). The gas abundances are calibrated using water equilibrated with air under known conditions of temperature, altitude, and humidity (typically 25 °C, 183 m, and 100% relative humidity). Typical sample size is 5 mL, and each analysis takes approximately 3 minutes. Samples are 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 water due to equilibration with the atmosphere and assimilation of excess air, similar to the method in (Beller et al., 2004). For the Burn Site wells, recharge temperature was determined based on dissolved xenon concentrations, and excess air was determined based on the concentration of neon. For wells where noble gases were not measured, the recharge temperature is assumed to be equal to the discharge temperature at the well, and argon was used to correct for excess air. Recharge elevations were assumed to be at the surface elevation of the well.

The decay of tritium (^3H) in groundwater and the subsequent accumulation of its daughter product, helium-3 (^3He), can be used to determine the age of a groundwater sample, i.e. the time since last equilibration of groundwater helium with atmospheric helium at recharge. The primary source of tritium in groundwater is recharging precipitation. Sources of helium in groundwater include equilibration with the atmosphere (for both ^3He and ^4He), the alpha decay

of uranium and thorium (for ^4He), and the beta decay of tritium (for ^3He). Distinguishing tritiogenic ^3He from non-tritiogenic ^3He in a groundwater sample typically requires the determination of other noble gases in the groundwater sample.

The Noble Gas Mass Spectrometer facility at LLNL has been operational for over fifteen 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 ^3He in-growth method (approximately 25 day accumulation time). Analytical uncertainties are approximately 1% for $^3\text{He}/^4\text{He}$, 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. Accurate $^3\text{H}/^3\text{He}$ ages can be determined if a samples contains more than 1 pCi/L of ^3H .

3 RESULTS

To date, eleven different wells have been sampled in the Burn Site area for analyses of groundwater age (Table 3a) and denitrification (Table 4). Depending on location, the wells are screened in Precambrian metasediments (phyllite and schist). Of the six wells that were sampled in 2012, all were resampled in 2015 with the exception of CYN-MW6 (Figure 2). Well CYN-MW15, located adjacent to CYN-MW6 but screened slightly deeper, was sampled in 2015 rather than CYN-MW6. Of the ten wells sampled in 2015, seven (CYN-MW9, CYN-MW10, CYN-MW11, CYN-MW12, CYN-MW13, CYN-MW14A, and CYN-MW15) contained groundwater with nitrate exceeding the 10 mg/L (as N) maximum concentration limit (MCL). Six of the seven wells with elevated nitrate are located in the central test area of the Burn Site and one well (CYN-MW13) is located approximately 2,000 feet west-southwest in the Lurance Canyon Arroyo. The groundwater age and nitrate isotope data are plotted on Figures 4 and 5, respectively.

The $^3\text{H}/^3\text{He}$ age-dating results indicate that the age of groundwater recharge varies across the study area. The two monitoring wells (CYN-MW9 and CYN-MW10) located near the Burn Site central test area that contain the highest nitrate concentrations (> 20 mg/L as N) also sample exclusively modern groundwater (< 50 years). Additionally, groundwater samples collected from wells CYN-MW9 exhibited a significant increase in the amount of tritium detected in 2015 compared to 2012 (Figure 4). The apparent $^3\text{H}/^3\text{He}$ age of the modern water in this well is less than 10 years. The increase in tritium concentration indicates an increase in the relative contribution of recent recharge. Wells CYN-MW11 and CYN-MW12 sampled predominantly fossil water with a small (< 1 pCi/L) but detectable modern component in 2012. However,

samples collected in 2015 contained significantly higher tritium concentrations, indicating a significant fraction of modern water. The other monitoring well (CYN-MW-13) that contains elevated nitrate (> 20 mg/L as N) also samples predominantly modern groundwater, in which a component of fossil water is also detected. All other groundwater monitoring wells that were sampled either contain exclusively fossil water or predominantly fossil water with a detectable modern component. Note that CYN-MW6, which was sampled in 2012 but not in 2015, contains predominantly modern water. As mentioned above, this well is located adjacent to CYN-MW15 but screened slightly shallower.

The $^3\text{H}/^3\text{He}$ method can only determine the average age of the groundwater and does not directly trace the source or age of the dissolved nitrate. In groundwater with a specific age (not-mixed) the age of the nitrate and the water are likely the same. In mixed-age groundwater, the age of the water and the mass-weighted age of the nitrate need not be the same. The results of a $^3\text{H}/^3\text{He}$ on a single mixed-age well cannot distinguish whether the high nitrate is associated with modern recharge. Monitoring wells CYN-MW11 and CYN-MW12, also located near the Burn Site central test area, contained very low but detectable amounts of modern recharge (< 1 pCi/L of ^3H). The farthest up gradient (CYN-MW4) and farthest down gradient monitoring wells (CYN-MW7 and CYN-MW8) contained pre-modern to fossil waters with no evidence of modern recharge and no detectable tritium (< 0.5 pCi/L). Although no $^3\text{H}/^3\text{He}$ ages could be calculated from these low-level tritium wells, the tritium data are supported by helium isotope ($^3\text{He}/^4\text{He}$) analyses. The monitoring wells with the lowest tritium concentrations also had the highest radiogenic ^4He concentrations. Based on the presence of radiogenic ^4He that accumulated in these samples from the decay of natural uranium and thorium, water from monitoring well CYN-MW4 is estimated to be on the order of several thousand years old, water from monitoring well CYN-MW7 is over 1,000 years old and CYN-MW8 is at least several hundred years old.

Denitrification in Burn Site groundwater is evaluated based on the presence of detectable excess nitrogen gas (N_2) and the isotopic composition of the nitrate. Although all six BSG AOC monitoring wells sampled in 2012 contained low but detectable levels of excess N_2 , only one well (CYN-MW11) contained detectable excess N_2 (4 +/-3 mg/L as N equivalent) in the 2015 groundwater sample. All 2012 detections of excess N_2 were close to the 2 mg/L as N equivalent detection limit, whereas the 2012 and 2015 results overlap within the uncertainty of this measurement. Additionally, ^{15}N and ^{18}O isotopes of nitrate were not significantly enriched in any of the groundwater samples collected in 2012 or 2015, with the exception of up gradient well CYN-MW4, which samples fossil water as shown in Figure 6 where nitrate concentration is plotted against $\delta^{15}\text{N-NO}_3$. Apparently, the fossil water in this well contained a low concentration of natural nitrate that has been almost completely denitrified. Although wells CYN-MW7 and CYN-MW8 contain low concentrations of nitrate (<10 mg/L as N) and CYN-MW7 contained detectable excess N_2 equivalent to 3 mg/L as N in the 2012 sample, the 2015 sample from CYN-MW7 did not contain detectable excess N_2 . Furthermore, neither well exhibits any evidence of isotopic enrichment indicative of denitrification.

The denitrification of nitrate in groundwater is typically favorable in oxygen-depleted groundwater systems with less than 2 mg/L of dissolved oxygen (DO). Groundwater from three monitoring wells (CYN-MW6, CYN-MW11, and CYN-MW12) have historically contained DO concentrations < 2 mg/L as measured in a flow cell during well purging for routine semiannual

sampling events. Groundwater monitoring wells CYN-MW4, CYN-MW7, and CYN-MW9 contained DO concentrations > 2 mg/L.

The isotopic composition of dissolved groundwater nitrate at the Burn Site for both 2012 and 2015 samples shown in Figures 5a and 5b indicate that most samples have isotopic compositions that fall within or close to the “Soil” source field, which represents nitrified soil nitrogen. The sample that falls furthest from the Soil source field is from the farthest up-gradient well, CYN-MW4, although the nitrate concentrations in well CYN-MW4 are very low and may be perturbed by small changes in $\delta^{15}\text{N-NO}_3$ to the nitrate isotopic composition during sample collection or transport. In Figure 6 nitrate concentration is plotted against $\delta^{15}\text{N-NO}_3$ and symbolized by groundwater age. Excluding CYN-MW4, the trend indicates wells that sample modern groundwater also contain the highest nitrate concentrations. The range of $\delta^{15}\text{N-NO}_3$ is consistent with nitrate soil sources and exhibits little evidence of isotopic enrichment related to denitrification. Although CYN-MW4 contains fossil groundwater slightly enriched in $\delta^{15}\text{N-NO}_3$, it is located up gradient of the Burn Site central test area and appears to be hydraulically isolated from modern recharge.

The stable isotopic composition of water was measured in all samples and plotted in Figure 7. Samples from all monitoring wells fall on or close to the Global Meteoric Water Line (GMWL) and do not show evidence for significant evaporation under hot arid conditions. The oxygen and hydrogen isotope compositions of CYN-MW9 changed significantly in the 2015 sample, consistent with modern recharge of isotopically distinct water.

Noble gas recharge temperatures (Table 3B) were calculated using a ground-surface elevation of 6,300 feet above mean sea level (Figure 6). Recharge temperatures of samples collected in 2015 agree well with 2012 results.

Figure 8 is a plot of $\delta^{18}\text{O-NO}_3$ isotopic composition plotted against $\delta^{18}\text{O-H}_2\text{O}$ isotopic composition. Nitrate produced by nitrification typically derives two oxygen atoms from air (which is isotopically uniform) and one oxygen atom from water (which varies). If nitrate is produced by nitrification with local water, then $\delta^{18}\text{O-NO}_3$ will fall on or close to a local water nitrification line. As shown in Figures 8, 11 of the 14 samples fall within two-sigma analytical uncertainty of the nitrification line and all but 3 of the samples fall with five-sigma analytical uncertainty of the nitrification line. Note that CYN-MW4 is not plotted on Figure 8.

4 CONCLUSIONS

Data from both the 2012 and 2015 sampling events are presented in Tables 3, 4, and 5. The interpreted groundwater age for each well is plotted on the BSG AOC map in Figure 9.

Based on these results, the conclusions of this groundwater denitrification and age dating study are:

- The highest NO_3 concentrations at the Burn Site (CYN-MW6, CYN-MW9, CYN-MW10) exhibit the youngest $^3\text{H}/^3\text{He}$ groundwater ages and the lowest tritogenic ^3He and

radiogenic ^4He concentrations. These wells sample water that is predominantly to exclusively modern (< 10 years).

- Groundwater from wells CYN-MW9, CYN-MW11, and CYN-MW12 collected in 2015 exhibited significant increases in the amount of tritium detected and changes in the oxygen and hydrogen isotope compositions when compared to the 2012 results. CYN-MW11 and CYN-MW12 sampled predominantly fossil water with a detectable modern component in 2012. The 2015 tritium concentrations in these wells indicate a significant increase in the relative contribution from recent recharge.
- The spatial and temporal correlation between modern groundwater and elevated nitrate suggest a significant vertical pathway for recharge that is likely co-located with an elevated nitrate source. The nitrate source could be natural, anthropogenic, or mixed. Given the complex hydrogeologic setting, the recharge pathway could be associated with faults or fracture corridors that act as vertical conduits for recharge to the deep bedrock aquifers. It is also possible that the annular seal(s) in one or more of the Burn Site wells have degraded and may be acting as vertical conduits for deep recharge.
- The lowest nitrate concentration wells (i.e., < 10 mg/L as N [the MCL]), CYN-MW4, CYN-MW7 and CYN-MW8, have the most radiogenic ^4He . These wells sample very old fossil water and represent levels that are indicative of natural background nitrate levels under past climatic and environmental conditions including water-rock interaction for at least several hundred years.
- The increased tritium concentrations in 2015, with respect to 2012, are evidence for recharge pathways at the Burn Site that are active under present day conditions.
- The combined results of the denitrification suite (i.e., low to non-detectable excess N_2 and no significant enrichment in nitrate isotopic composition) are not supportive of any significant natural attenuation of groundwater nitrate in the Burn Site monitoring wells.

Table 3A Groundwater Age Data

n.s. = not sampled

Well ID	Tritium pCi/L 2012	+/-	Terrigenic He 10 ⁻⁹ cm ³ STP/g 2012	+/-	Tritium pCi/L 2015	+/-	Terrigenic He 10 ⁻⁹ cm ³ STP/g 2015	+/-	Interpreted Groundwater Age 2012	Interpreted Groundwater Age 2015
CYN-MW4	< 0.5	0.14	326.7	8.5	< 0.5	0.07	140.5	4.3	Fossil	Fossil
CYN-MW6	3.49	0.87	< 3	1.5	n.s.		n.s.		Modern	n.s.
CYN-MW7	< 0.5	0.60	149.6	4.4	< 0.5	0.09	121.3	3.8	Fossil	Fossil
CYN-MW8	n.s.		n.s.		< 0.5	0.32	50.3	4.4	n.s.	Fossil
CYN-MW9	3.26	0.24	7.4	1.7	10.7	0.59	< 3.2	1.6	Modern w/det Fossil	Modern
CYN-MW10	n.s.		n.s.		3.1	0.34	< 3.2	1.6	n.s.	Modern
CYN-MW11	0.30	0.79	41.4	2	1.7	0.29	35.2	2	Fossil w/det Modern	Fossil w/det Modern
CYN-MW12	0.46	0.89	40.6	2.3	4.7	0.24	31.7	2.1	Fossil w/det Modern	Fossil w/det Modern
CYN-MW13	n.s.		n.s.		6.2	0.30	6.2	1.7	n.s.	Modern w/det Fossil
CYN-MW13 (dup)	n.s.		n.s.		6.0	0.28	8.2	1.6	n.s.	Modern w/det Fossil
CYN-MW14A	n.s.		n.s.		2.1	0.20	15.3	1.9	n.s.	Fossil w/det Modern
CYN-MW15	n.s.		n.s.		2.5	0.31	69	2.9	n.s.	Fossil w/det Modern

Table 3B Noble Gas Recharge Temperatures

Burn Site Well	NGRT °C 2012	+/-	NGRT °C 2015	+/-
CYN-MW4	12.7	1.0	12.9	1.0
CYN-MW6	19.4	1.1	21.4	1.2
CYN-MW7			18.5	1.3
CYN-MW8	17.6	1.1	16.5	1.1
CYN-MW9			16.0	1.1
CYN-MW10	17.9	1.1	15.7	1.0
CYN-MW11	15.5	1.1	16.1	1.1
CYN-MW12			19.0	1.1
CYN-MW13			18.3	1.1
CYN-MW13 (dup)			17.9	1.1
CYN-MW14A			16.0	1.1
CYN-MW15	12.7	1.0	12.9	1.0

Table 4 Denitrification Data

Well ID	$\delta^{15}\text{N-NO}_3$ air 2012	$\delta^{18}\text{O-NO}_3$ SMOW 2012	$\delta^{15}\text{N-NO}_3$ air 2015	$\delta^{18}\text{O-NO}_3$ SMOW 2015	Excess N_2 (as N) 2012	+/-	Excess N_2 (as N) 2015	+/-
CYN-MW4	12.3	17.6	10.4	-6.6	3	2	< 2	4
CYN-MW6	5.9	-0.4	n.s.	n.s.	5	3	n.s.	
CYN-MW7	5.2	0.7	5.1	1.4	3	3	< 2	3
CYN-MW8	n.s.	n.s.	4.9	1.8	n.s.		< 2	7
CYN-MW9	2.1	0.0	2.4	-1.7	3	1	< 2	3
CYN-MW10	n.s.	n.s.	2.4	0.7	n.s.		< 2	3
CYN-MW11	5.9	3.4	3.7	2.2	4	1	4	3
CYN-MW12	5.0	1.6	4.7	2.9	3	1	< 2	3
CYN-MW13	n.s.	n.s.	3.7	2.4	n.s.		< 2	3
CYN-MW13 (dup)	n.s.	n.s.	3.1	3.0	n.s.		< 2	3
CYN-MW14A	n.s.	n.s.	4.6	1.8	n.s.		< 2	3
CYN-MW15	n.s.	n.s.	4.7	2.9	n.s.		< 2	3

Table 5 Water Isotope Data

Burn Site Well	$\delta^{18}\text{O-H}_2\text{O}$ 2012	$\delta\text{D-H}_2\text{O}$ 2012	$\delta^{18}\text{O-H}_2\text{O}$ 2015	$\delta\text{D-H}_2\text{O}$ 2015
CYN-MW4	-11.6	-83	-11.2	-83
CYN-MW6	-9.9	-71	n.s.	n.s.
CYN-MW7	-10.7	-77	-10.1	-77
CYN-MW8	n.s.	n.s.	-10.1	-78
CYN-MW9	-10.8	-74	-9.2	-65
CYN-MW10	n.s.	n.s.	-10.6	-78
CYN-MW11	-11.0	-78	-10.5	-77
CYN-MW12	-11.0	-77	-10.4	-78
CYN-MW13	n.s.	n.s.	-9.1	-66
CYN-MW13 (dup)	n.s.	n.s.	-9.1	-63
CYN-MW14A	n.s.	n.s.	-10.4	-78
CYN-MW15	n.s.	n.s.	-10.4	-76

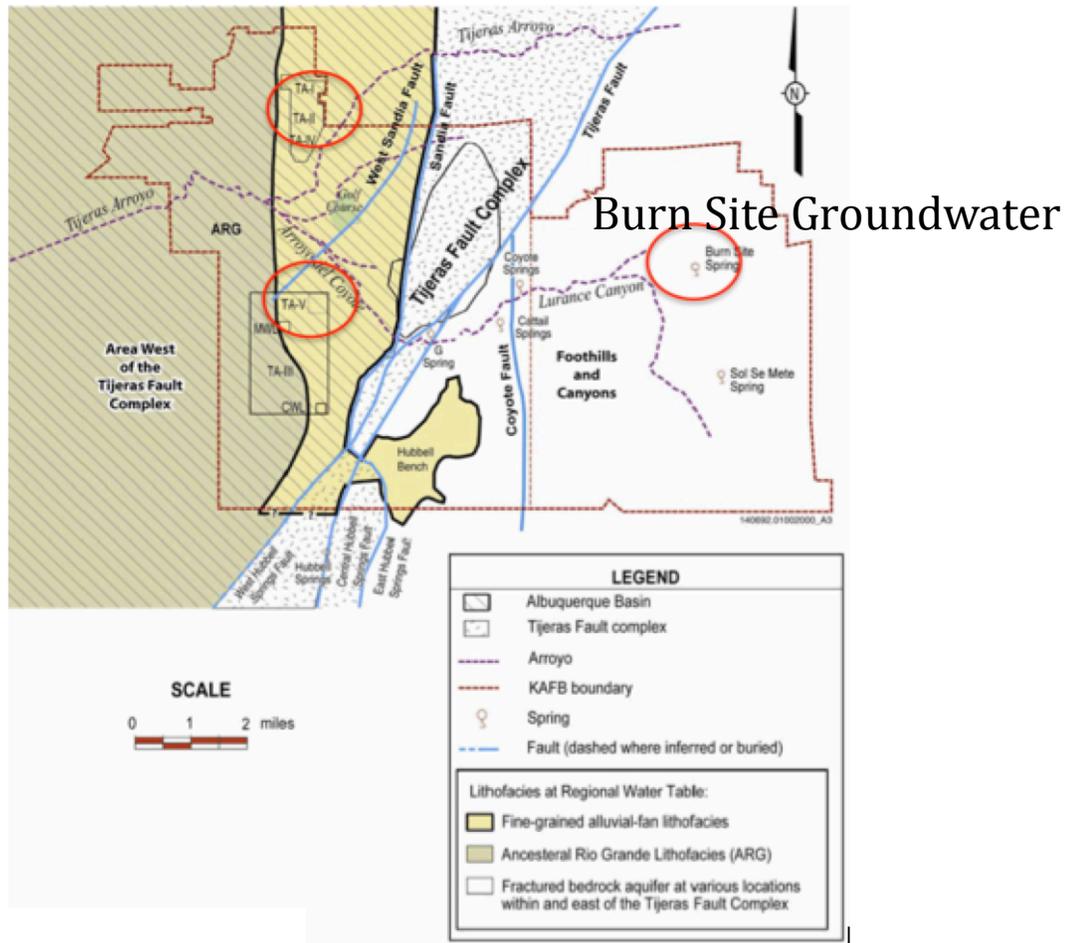


FIGURE 1. Generalized hydrogeologic map of the Albuquerque area showing the three Sandia National Laboratories/New Mexico Areas of Concern sampled in 2012. In 2015 groundwater samples were collected from the BSG AOC only.

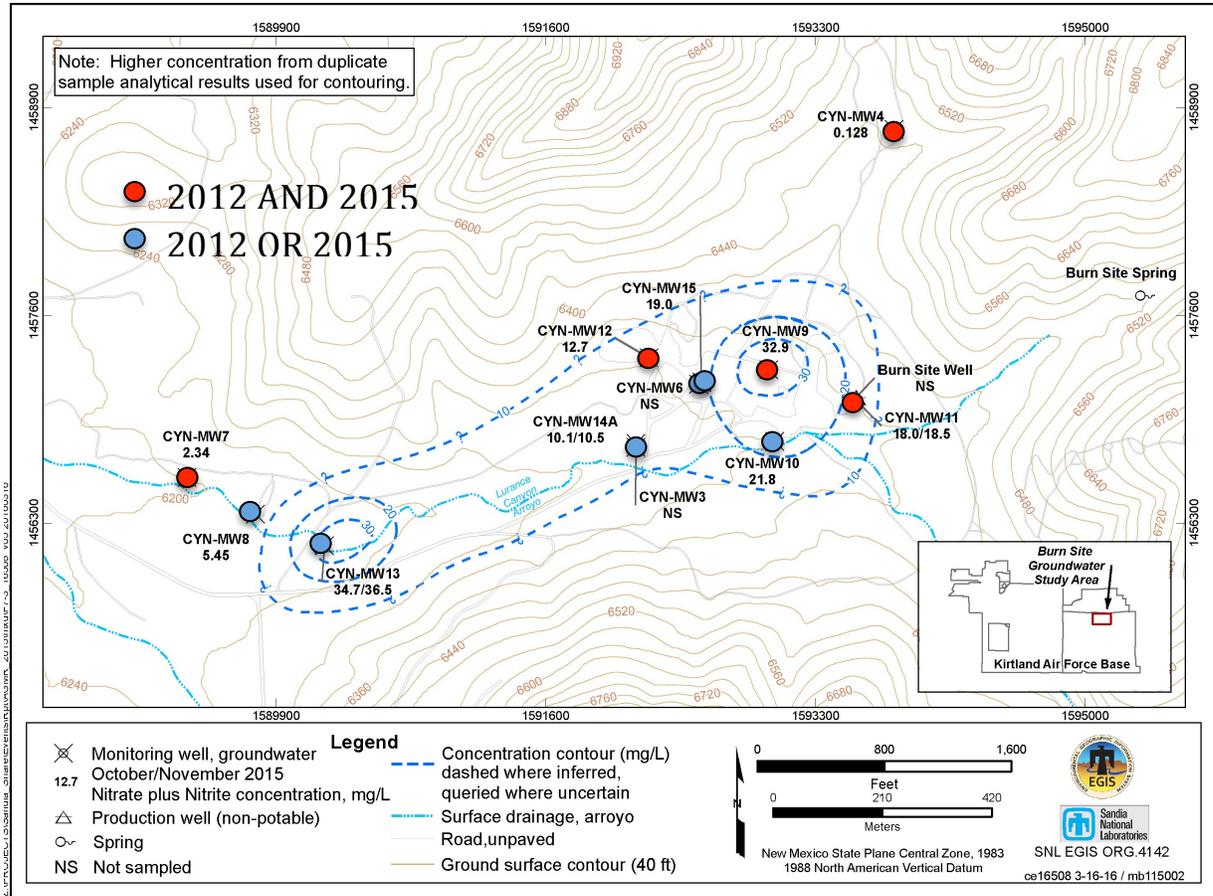


FIGURE 2. Site map showing all wells sampled at the BSG AOC and annotated to indicate which wells were sampled in 2012 and 2015.

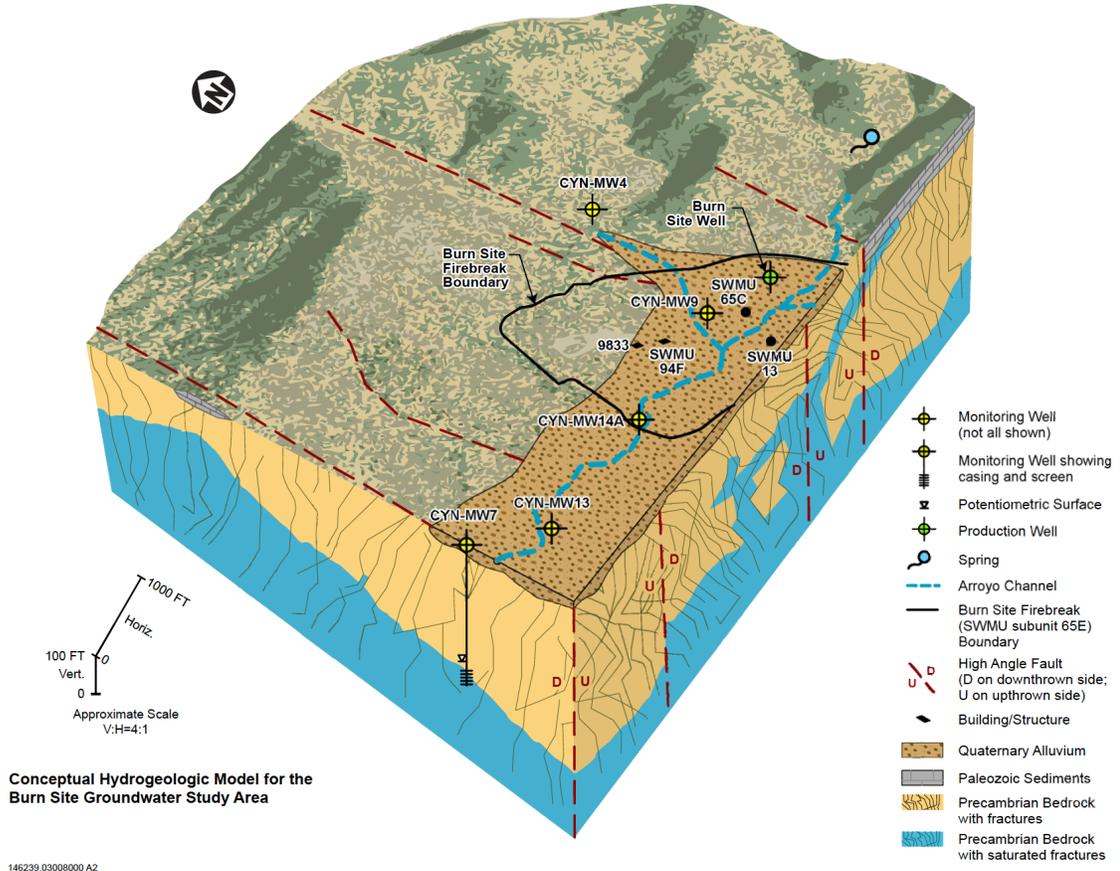


FIGURE 3. Sandia National Laboratories/New Mexico Conceptual Hydrogeologic Model for the BSG AOC.

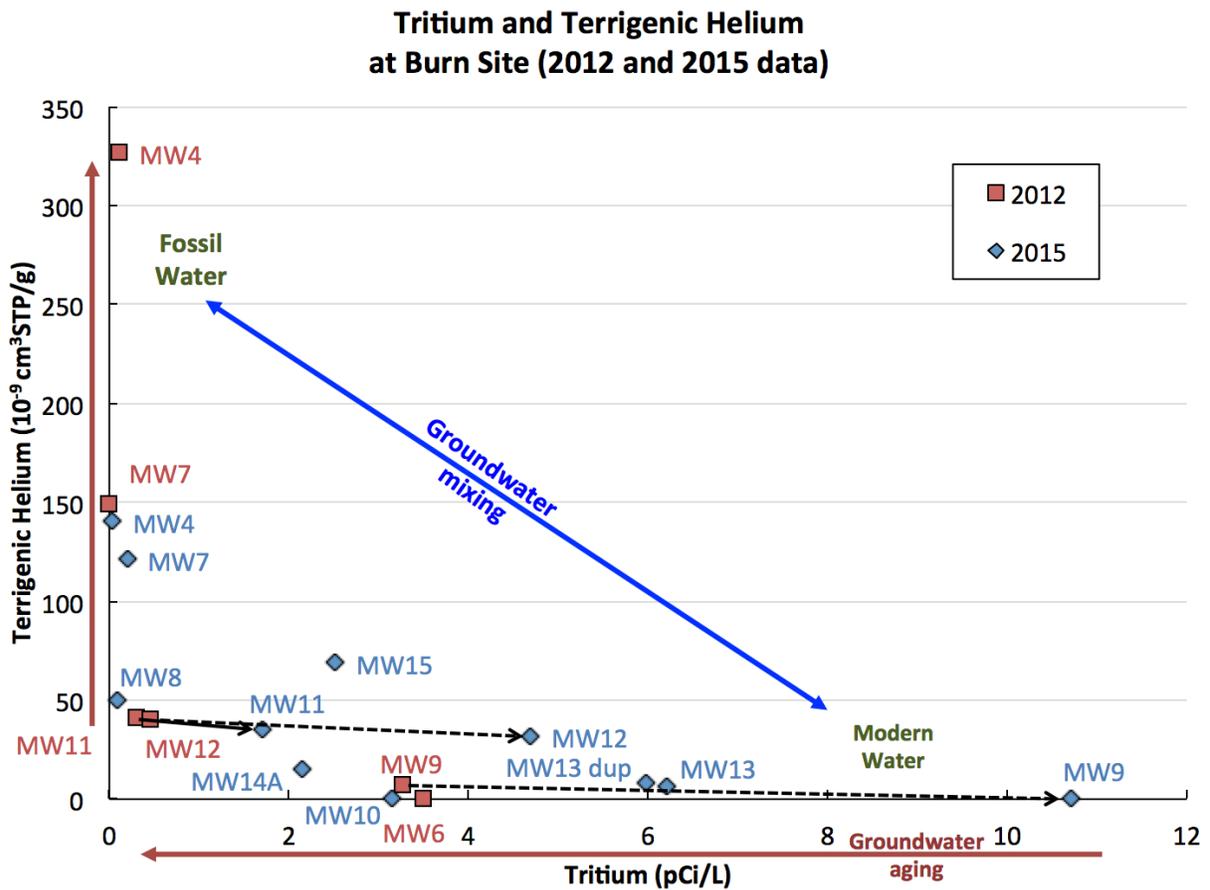


FIGURE 4. Plot of Terrigenous Helium versus Tritium for all BSG AOC groundwater samples collected in 2012 and 2015. The well prefix CYN- is not shown for spacing considerations.

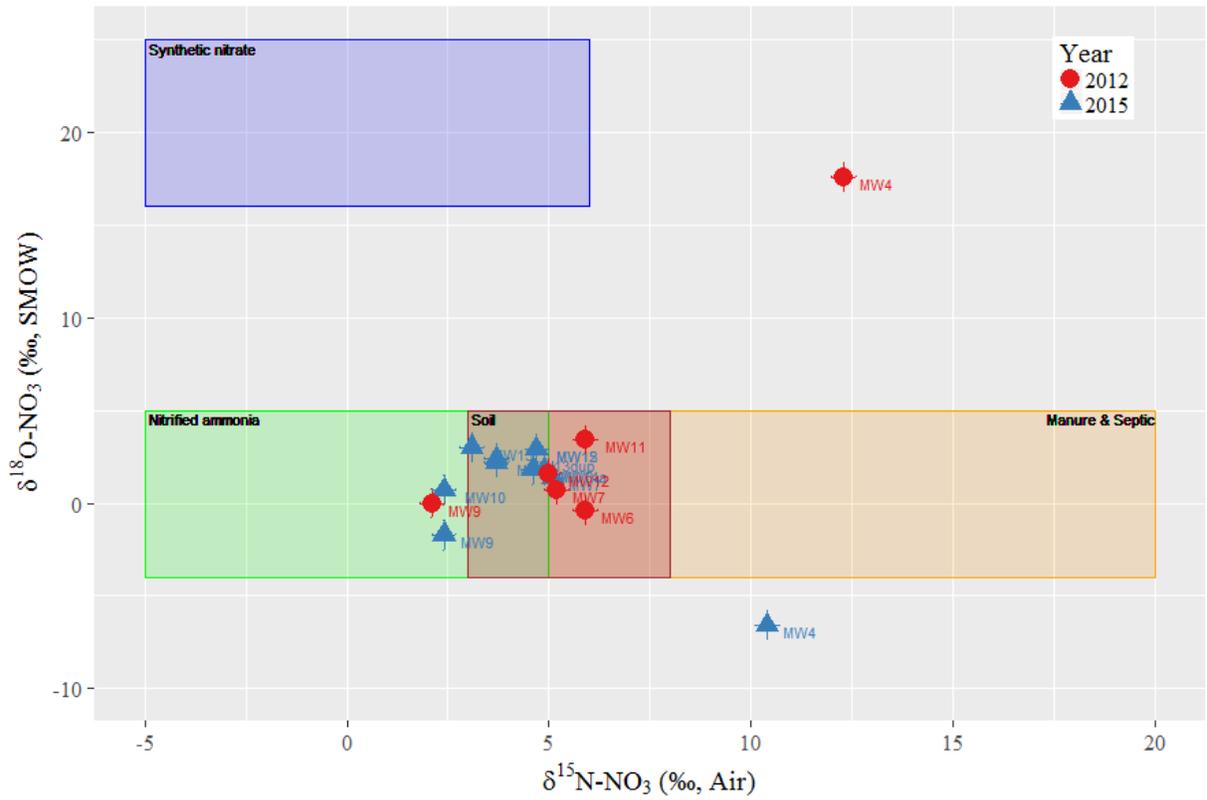


FIGURE 5a. Plot of $\delta^{15}\text{N-NO}_3$ vs $\delta^{18}\text{O-NO}_3$ for all BSG AOC groundwater samples collected in 2012 and 2015. Source fields (boxes) derived from Kendall (1998).

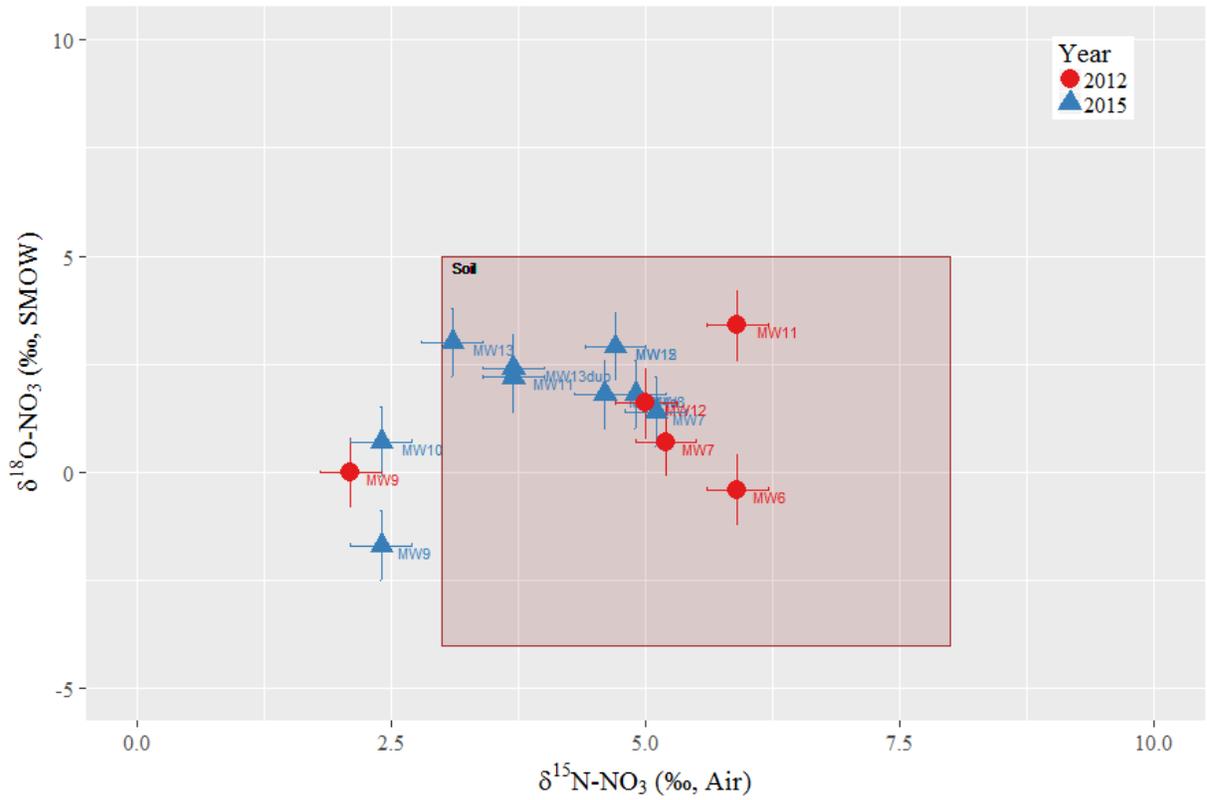


FIGURE 5b. Expanded plot of $\delta^{15}\text{N-NO}_3$ vs $\delta^{18}\text{O-NO}_3$ for BSG AOC groundwater samples collected in 2012 and 2015. Soil source field derived from Kendall (1998).

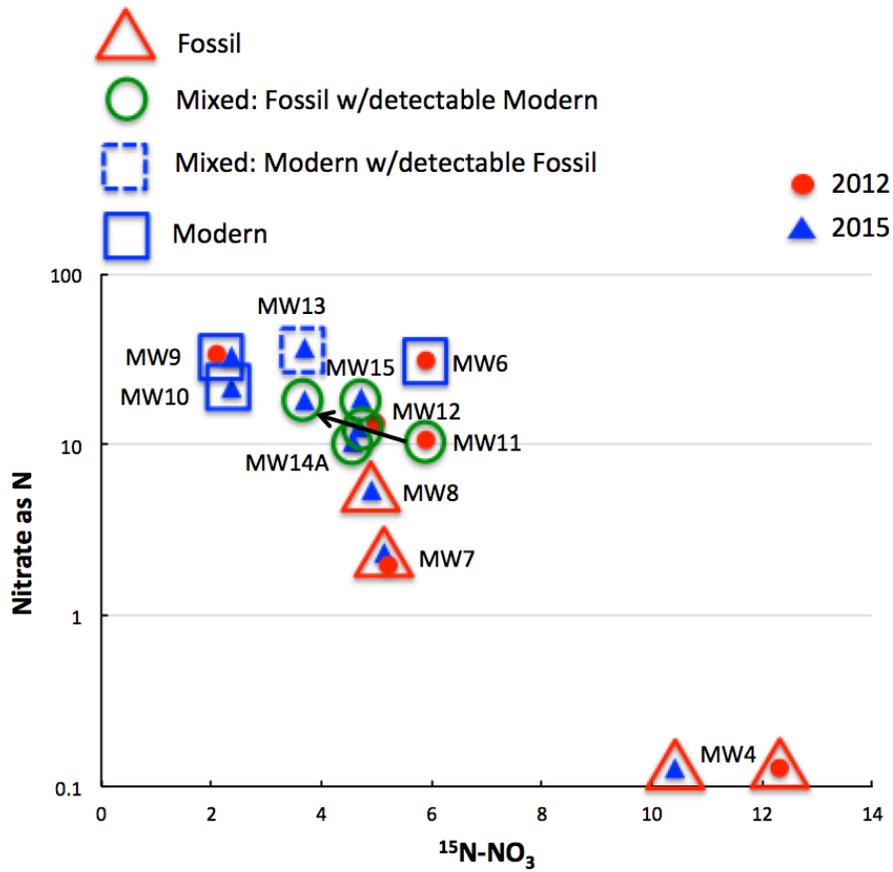


FIGURE 6. Plot of Nitrate in mg/L as N vs ¹⁵N-NO₃ annotated with groundwater age for all BSG AOC samples collected in 2012 and 2015.

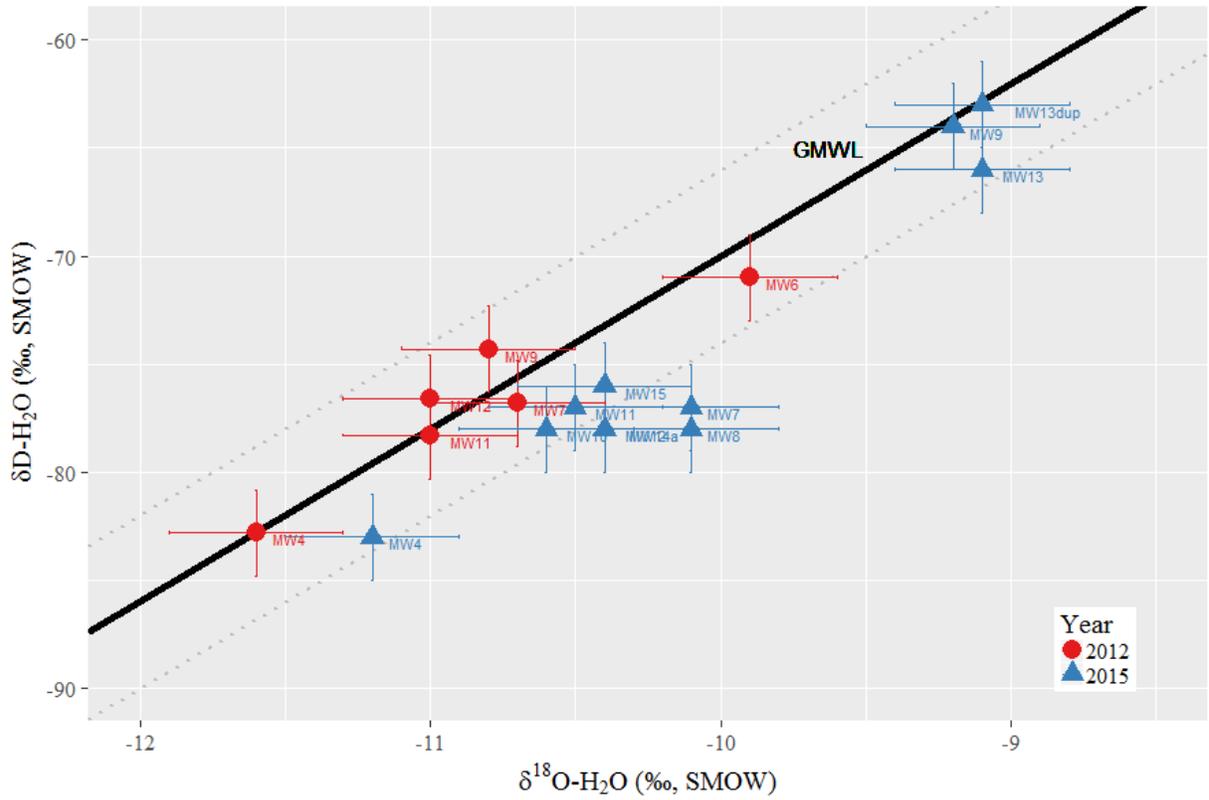


FIGURE 7. Isotopic composition of water with Global Meteoric Water Line (GMWL) from BSG AOC groundwater samples collected in 2012 and 2015. Note CYN-MW4 is not shown on the plot.

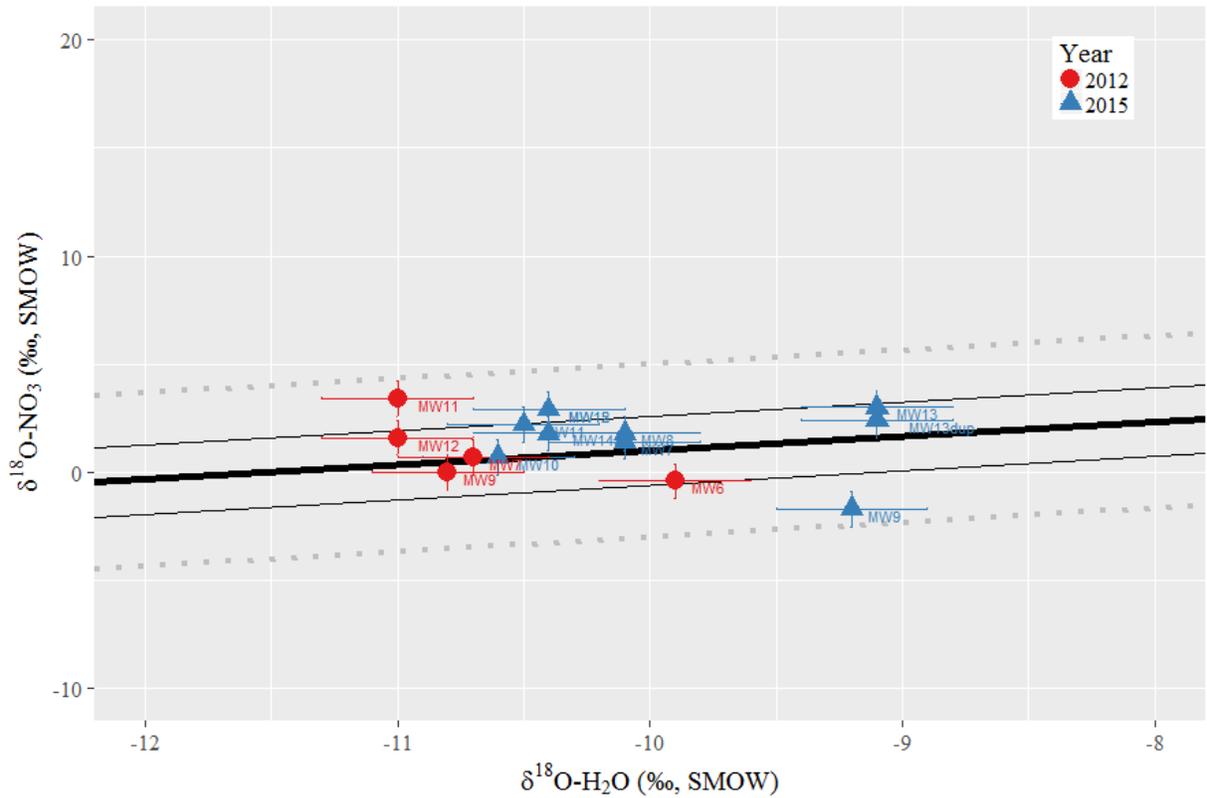


FIGURE 8. Isotopic composition of $\delta^{18}\text{O-NO}_3$ plotted against isotopic composition of $\delta^{18}\text{O-H}_2\text{O}$ for BSG AOC groundwater samples. The expected correlation for nitrification with local water is shown as a thick black line with two-sigma (thin black lines) and five-sigma (dotted lines) analytical uncertainty. This correlation assumes that two of the three oxygen atoms in the nitrate molecule come from air and one comes from local water. Note CYN-MW4 is not shown on the plot.

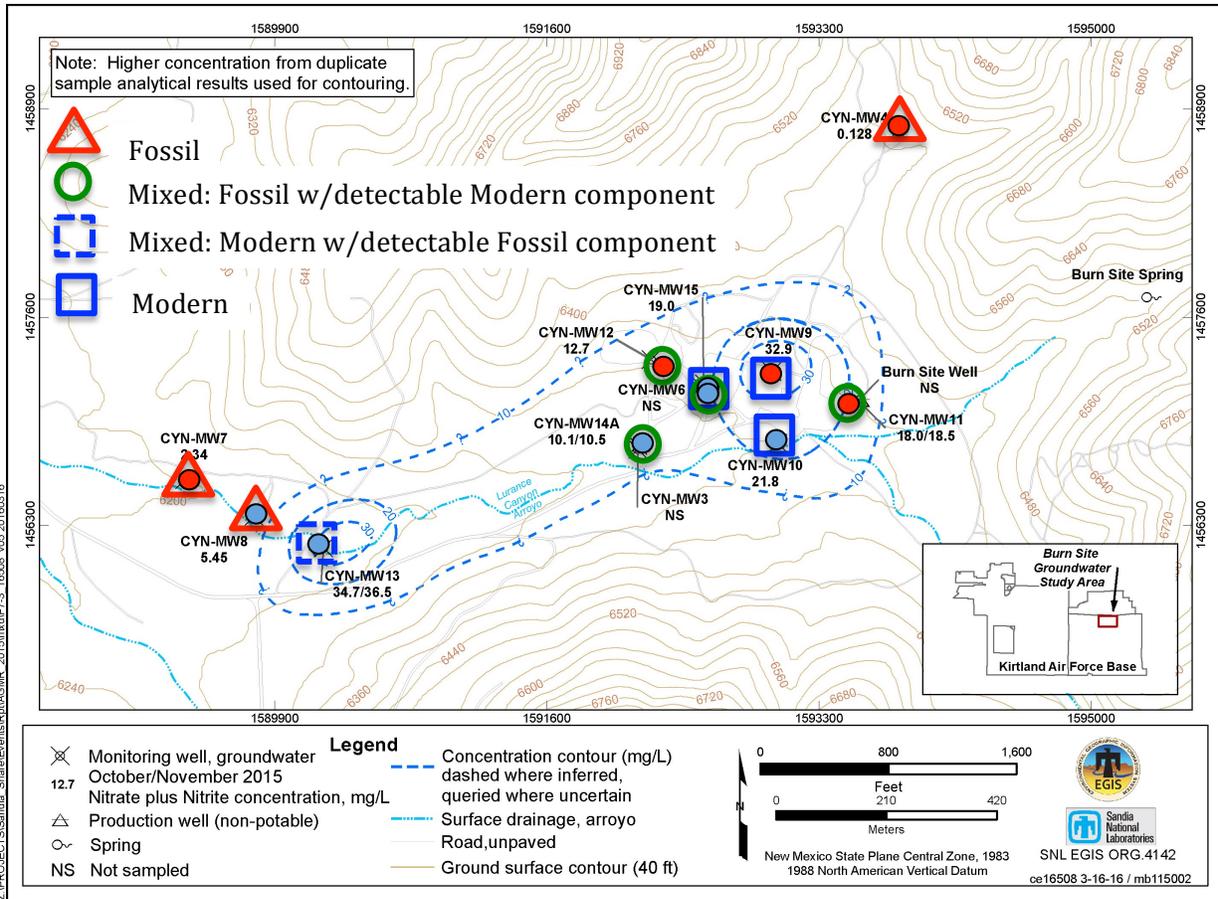


FIGURE 9. Summary map showing groundwater age on the 2015 BSG AOC nitrate distribution.

5 REFERENCES

- Beller, H.R., Madrid, V.M., Hudson, G.B., McNab, W.W., Carlsen, T., 2004. Biogeochemistry and natural attenuation of nitrate in groundwater at an explosives test facility. *Applied Geochemistry* 19, 1483-1494.
- Casciotti, K.L., Sigman, D.M., Hastings, M.G., Bohlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry* 74, 4905-4912.
- Epstein, S., Mayeda, T.K., 1953. Variation of O-18 content of waters from natural sources. *Geochim. Cosmochim. Acta* 4, 213-224.
- Jackson, T., Lauffer, F., Mitchell, M., Skelly, M., 2011. Sandia National Laboratory Annual Groundwater Monitoring Report (Calendar Year 2010). Groundwater Protection Program; Sandia National Laboratories, New Mexico.
- Kana, T.M., Darkangelo, C., Hunt, M.D., Oldham, J.B., Bennett, G.E., Cornwell, J.C., 1994. Membrane inlet mass spectrometer for rapid high precision determination of N₂, O₂, and Ar in environmental water samples. *Analytical Chemistry* 66, 4166-4170.
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier Science, Amsterdam, pp. 519–576.
- Lambert S. J. and Balsley S. D. (1997) Stable-isotopes of groundwaters from the Albuquerque, New Mexico, basin: one decade later. *Environmental Geology* 31, 199–204.
- Madrid, V.M., Singleton, M.J., Visser, A., and Esser, B.K. (2013) Summary of isotopic data and preliminary interpretation of denitrification and age-dating for groundwater samples from three Sandia National Laboratory (SNL) sites. Lawrence Livermore National Laboratory LLNL-SR-636381, 19 pp.
- Morrison, J., Brockwell, T., Merren, T., Fourel, F., Phillips, A.M., 2001. On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. *Analytical Chemistry* 73, 3570-3575.
- Plummer L. N., Bexfield L. M., Anderholm S. K., Sanford W. E. and Busenberg E. (2012) Geochemical Characterization of Ground-water Flow in the Santa Fe Group Aquifer System, Middle Rio Grande Basin, New Mexico. *U.S. Geological Survey Water-Resources Investigations Report 03-4131 (Version 1.2)*. Available at: <http://pubs.usgs.gov/wri/wri034131/>
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., Bohlke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical Chemistry* 73, 4145-4153.
- Singleton, M.J., Esser, B.K., Moran, J.E., Hudson, G.B., McNab, W.W., Harter, T., 2007. Saturated zone denitrification: Potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science & Technology* 41, 759-765.
- Singleton, M.J., Woods, K.N., Conrad, M.E., Depaolo, D.J., Dresel, P.E., 2005. Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable

isotopes at the Hanford Site, Washington. *Environmental Science & Technology* 39, 3563-3570.

Visser, A., Hillegonds, D., Esser, B.K., 2013a. Collection and Analysis of Groundwater for Determination of Noble Gas Abundance and Helium Isotopic Composition (SOP-NGMS-122 revision 4). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623335), p. 15.

Visser, A., Hillegonds, D., Esser, B.K., 2013b. Collection and Analysis of Groundwater for Determination of Tritium by Helium-3 Accumulation (SOP-NGMS-121 revision 4). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623415), p. 9.