Perchlorate at Basalt and Vine Tree springs on San Ildefonso Pueblo land

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Introduction

The perchlorate concentration at Basalt and Vine Tree springs on San Ildefonso Pueblo have been near or above the 4 µg/L Consent Order screening level since August 2008 (Figure 1).

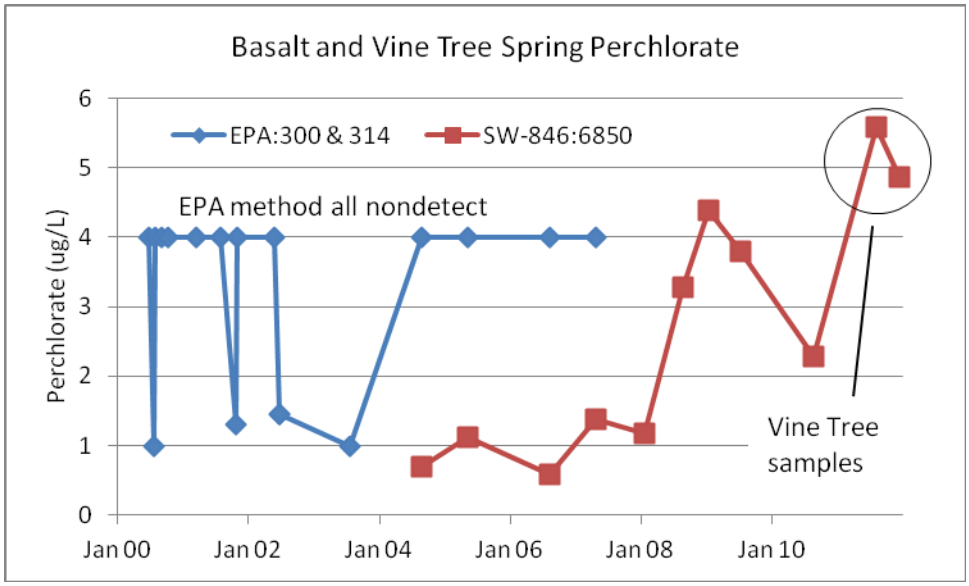


Figure 1. Perchlorate concentration history at Basalt and Vine Tree springs. Note that all EPA method results are nondetect.

This summary looks at the setting of the springs, the perchlorate concentration history, and perchlorate concentrations at upgradient locations. Perchlorate was used as an oxidizing agent in radiochemistry at Los Alamos National Laboratory (LANL). Possible perchlorate sources include discharges from former radioactive industrial waste water treatment plants. One treatment plant discharged into Acid Canyon, a tributary of Pueblo Canyon, from 1943 to 1964. Another treatment plant discharged into DP Canyon, a Los Alamos Canyon tributary, from 1952 to 1986.

Basalt Spring has been sampled since the 1940s at part of the LANL environmental monitoring network. Purtymun (1995) described this spring as a discharge point for perched intermediate groundwater (Figures 2 and 3) that was also observed in Pueblo Canyon wells.

Basalt Spring discharges just above the level of the stream in Los Alamos Canyon. In 2010, Pueblo personnel noted that this spring had dried up. Discharge appeared a short distance downstream and this new location is called Vine Tree Spring. This new location was sampled as an alternate in 2011.

Perchlorate Data

LANL began measuring perchlorate in about 2000. Early results were measured with EPA methods 300 and 314, which use ion chromatography (IC). The nominal method detection limit (MDL) for these

methods is 4 µg/L, though lower numbers were often reported. Because analytical laboratories did not apply all the steps in these methods, IC measurements often suffered great inaccuracy. The perchlorate peak can be masked by interference by other ions, particularly sulfate, which elutes at the same time as perchlorate. The perchlorate IC results are unusable in this concentration range, as shown below where parallel results are available.

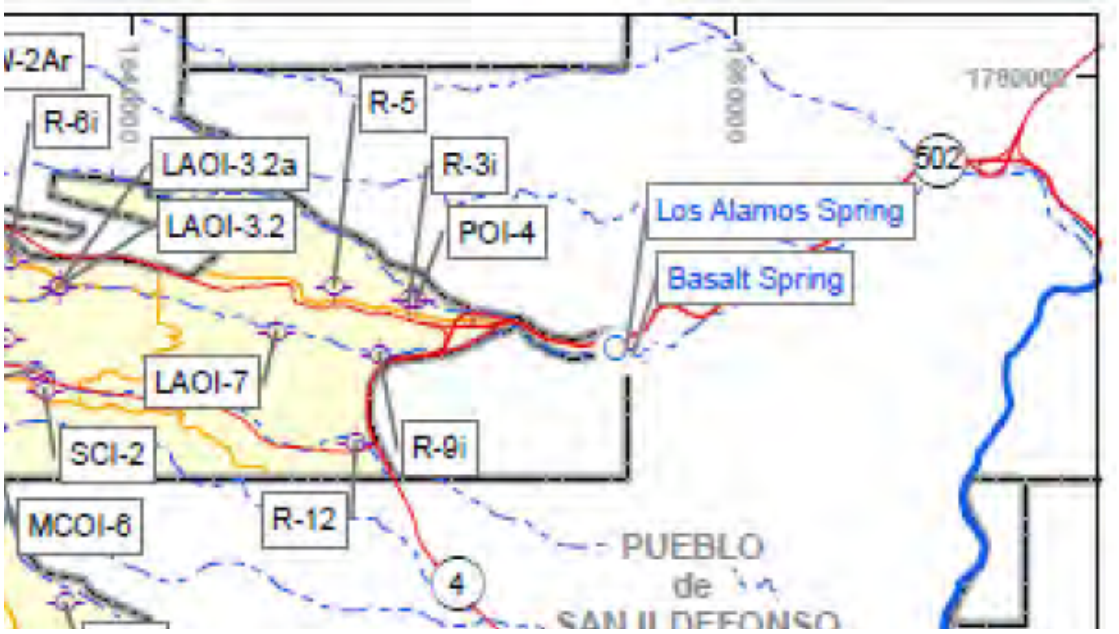
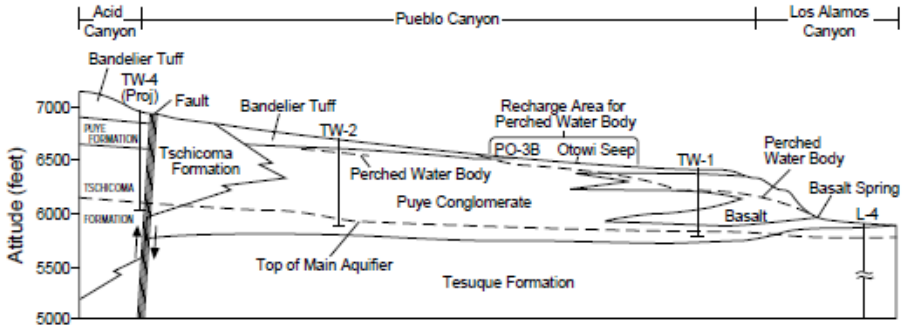


Figure 2. Location of Basalt Spring. Vine Tree Spring is next to Basalt Spring. The map shows locations for other wells mentioned in the text.



Map with cross section along Pueblo Canyon showing perched water in volcanic sediments in the middle and lower reaches of Pueblo Canyon.

Figure 3. Cross section of Pueblo and part of Los Alamos Canyon (Purtymun, 1995).

A new method, SW-846:6850, using liquid chromatography/mass spectrometry/ mass spectrometry (LC/MS/MS) came into use about 2002 and became a promulgated method in about 2007. The MDL for SW-846:6850 and variants is 0.05 µg/L, an 80-fold improvement over EPA:314.

The following review of perchlorate concentrations at surface water and groundwater monitoring locations upgradient of Basalt and Vine Tree springs shows that most of the closest locations have lower perchlorate concentrations and do not show increases since 2007.

Pueblo Canyon Locations

Two Pueblo Canyon surface water locations showed high perchlorate concentrations measured with the IC method in 2006 and 2007, but LC/MS/MS results were much lower. Pueblo above SR-502 had IC results of 4.8 µg/L to 5.5 µg/L in 2006 and 2007. The LC/MS/MS results on the same dates are nondetect (< 0.05 µg/L) and 0.11 µg/L. The IC results since 2006 and are below 2 µg/L (Figure 4). At Pueblo 3 (located about 1 mile above SR-502), IC results in 2007 were 25.8 µg/L and 17 µg/L (Figure 5). The LC/MS/MS results on the same dates are nondetect (< 0.05 µg/L) and 0.11 µg/L. Once again, the LC/MS/MS results on the same dates are 0.11 µg/L and nondetect (< 0.05 µg/L).

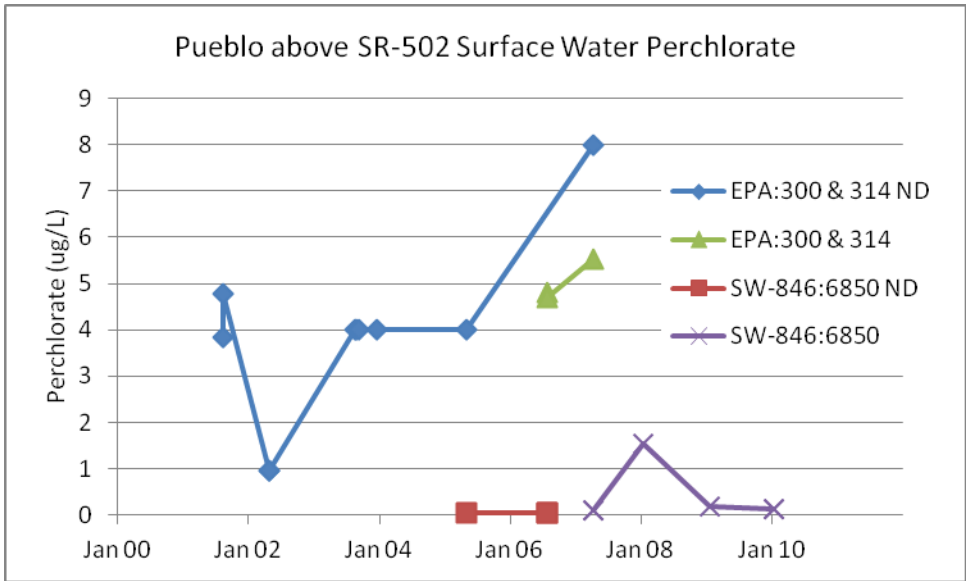


Figure 4. Perchlorate concentrations at Pueblo above SR-502. Note that most EPA method results are nondetect (ND) or negated by LC/MS/MS results on the same date.

At Pueblo Canyon intermediate well POI-4 (depth 159 ft) perchlorate was not detected by the IC method. The LC/MS/MS results have an average concentration of 0.29 µg/L (Figure 6). At nearby intermediate well R-3i (depth 215 ft) there is one IC detect of 4.5 µg/L, which is estimated (that is, just above the detection limit and not quantifiable). However, the LC/MS/MS result on that date was 2.5 µg/L. The remaining LC/MS/MS results have an average concentration of 2.7 µg/L, aside from a low initial result (Figure 7).

Regional well R-4 (depth 793 ft) is another location in Pueblo Canyon that shows higher perchlorate concentrations (Figure 8). The LC/MS/MS results since 2008 have an average concentration of 4.58 µg/L. Some lower earlier values decrease the average for all LC/MS/MS results to 4.18 µg/L. The IC detections at this well are all estimated values. Another regional aquifer well in Pueblo Canyon of note

is water supply well Otowi-1, where LC/MS/MS results have generally fallen from 3 µg/L to 1 µg/L since 2004.

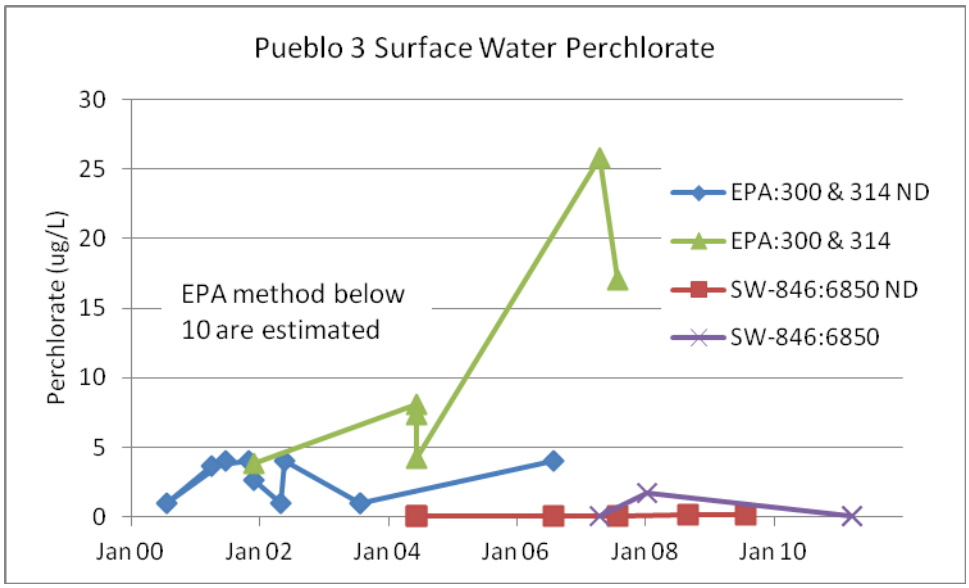


Figure 5. Perchlorate concentrations at Pueblo 3.

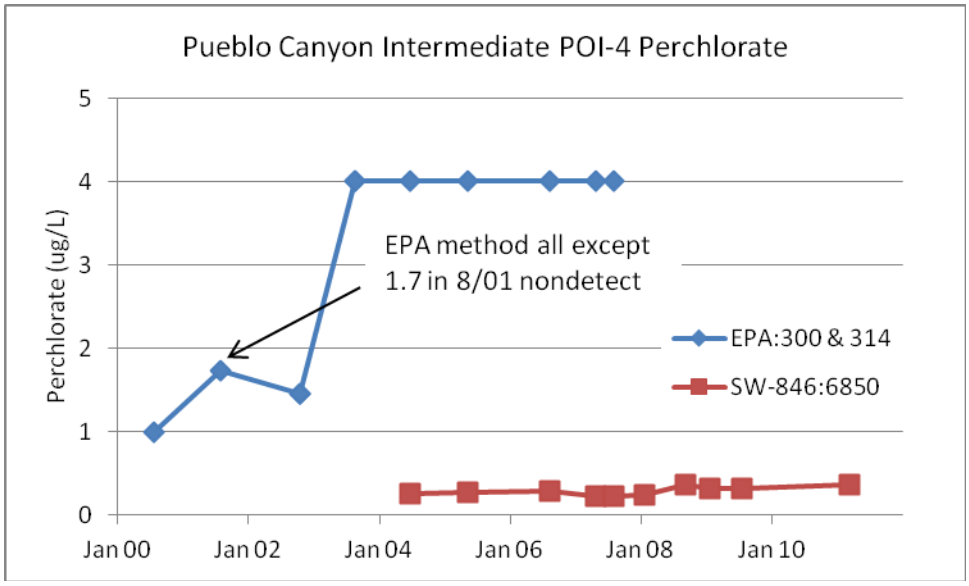


Figure 6. Perchlorate concentrations at POI-4.

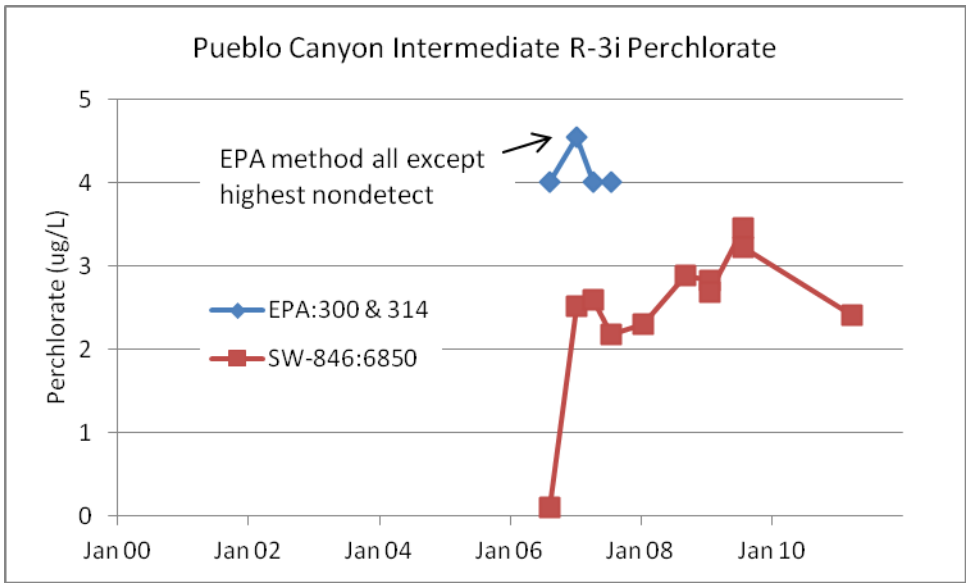


Figure 7. Perchlorate concentrations at R-3i.

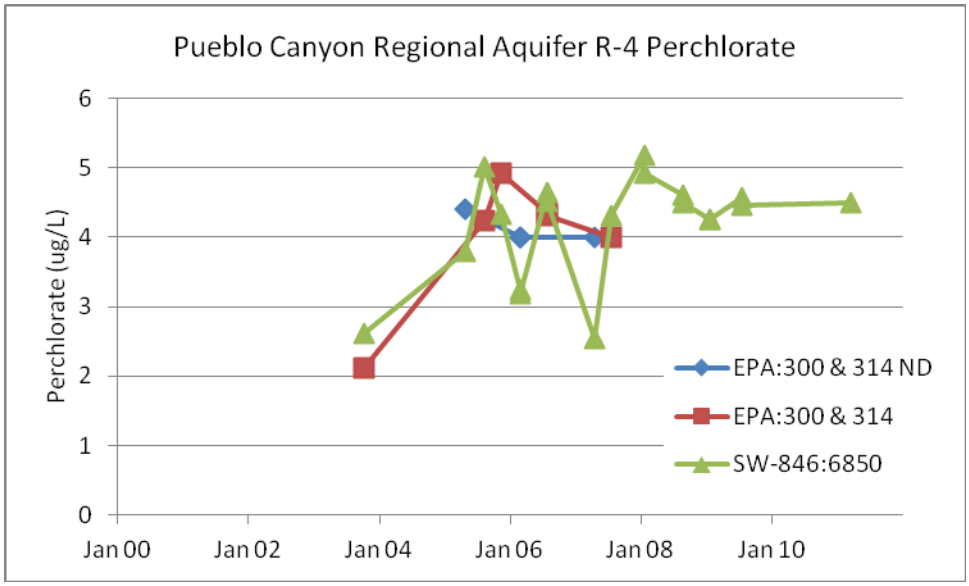


Figure 8. Perchlorate concentrations at R-4.

Los Alamos and Sandia Canyon Locations

Several surface water locations in Los Alamos Canyon have perchlorate measurements, but none after April 2007. The locations Los Alamos above SR-4 and Los Alamos below LA Weir have IC results in March 2001 of near 11 µg/L and another at the latter location of 6.7 µg/L. These values are questionable due to analytical problems with this method in this time frame. At Los Alamos above SR-4 in April 2005 there is an IC result of 30.2 µg/L; the LC/MS/MS result on this date is 0.405 µg/L, contradicting the IC result. The LC/MS/MS values for these locations in 2005 and 2007 were all below 0.5 µg/L.

At Los Alamos Canyon intermediate well R-9i, the 2005 and 2008 LC/MS/MS values at the 199 ft screen were 0.2 µg/L. Perchlorate concentrations at the 279 ft screen are higher, with LC/MS/MS values averaging 2.20 µg/L (Figure 9). Three intermediate wells located farther up Los Alamos Canyon (LAOI-3.2, LAOI-3.2a, and R-6i) have perchlorate concentrations that range from 3 µg/L to 8 µg/L since 2005. The concentrations at these wells have generally declined, with R-6i (the highest) dropping to near 6.4 µg/L in 2011.

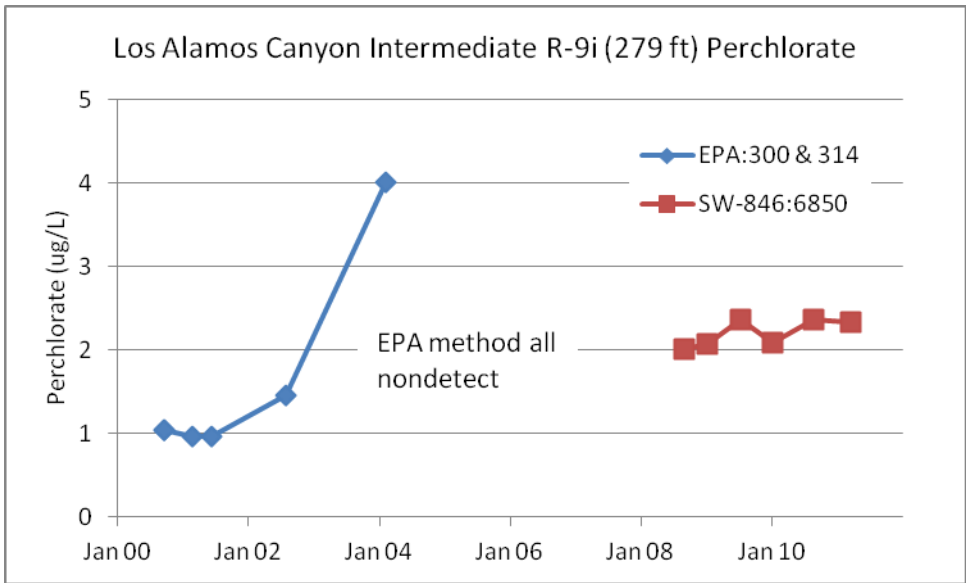


Figure 9. Perchlorate concentrations at the 279 ft screen of R-9i.

For Sandia Canyon intermediate well R-12, the LC/MS/MS values at the 459 ft screen average 2.86 µg/L since 2008. Perchlorate concentrations at the 505 ft screen are higher, with LC/MS/MS values averaging 1.0 µg/L (Figure 10), aside from a low initial result.

LC/MS/MS perchlorate concentrations in Sandia Canyon surface water and alluvial groundwater samples since 2007 show an annual cycle. At the surface water location named Sandia right fork at Power Plant, the perchlorate concentration on February 1, 2010 was 5.8 µg/L. At two surface water locations farther downstream, unusually high concentrations of perchlorate were seen in late 2009 and early 2010. The concentration on November 3, 2009, in alluvial well SCA-2 reached 2.7 µg/L. The perchlorate concentration was 5.2 µg/L on November 23, 2009, in a sample taken from the Power Plant outfall (EPA NPDES outfall 1) by the NMED Oversight Bureau. This suggests that variation in downstream surface and groundwater concentrations is caused by effluent perchlorate concentration variation.

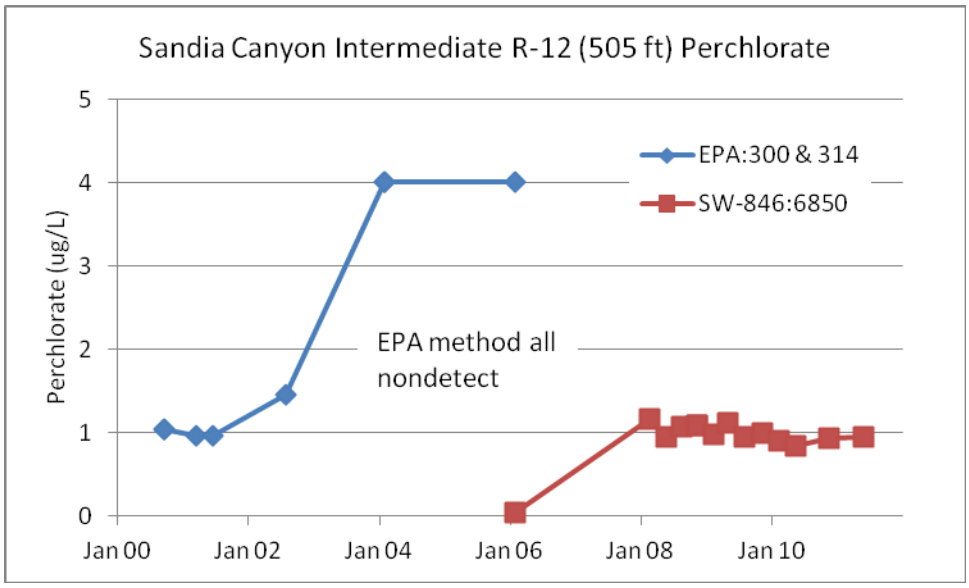


Figure 10. Perchlorate concentrations at the 505 ft screen of R-12.

Conclusion

An unknown amount of perchlorate was released by radioactive industrial outfalls in Pueblo Canyon (ending in 1964) and DP Canyon (ending in 1986). Since that time most of the perchlorate has been removed from the groundwater system due to its solubility and to cessation of discharges. The perchlorate concentrations observed today (except for that from the outfall in Sandia Canyon) are likely to be the remnant of earlier effluent and are decreasing with time.

Perchlorate samples analyzed by LC/MS/MS since about 2004 are most reliable for evaluating concentrations in the 4 µg/L to 5 µg/L range observed recently at Basalt and Vine Tree Springs. A few locations show earlier results measured by IC but these are of doubtful accuracy due to problems with early analyses with this method. Upgradient locations showing perchlorate concentrations in the range of recent values at Basalt and Vine Tree Springs included Pueblo Canyon intermediate well R-3i (2.7 µg/L), Pueblo Canyon regional aquifer well R-4 (4.18 µg/L), the 279 ft screen at Los Alamos Canyon intermediate well R-9i (2.2 µg/L), and three intermediate wells farther up Los Alamos Canyon (LAOI-3.2, LAOI-3.2a, and R-6i) that show concentrations that range from 3 µg/L to 8 µg/L. In Sandia Canyon, outfall and surface water samples have concentrations in the past few years up to 5.8 µg/L.

The precise flow path of water discharging at Basalt and Vine Tree Springs is uncertain. The discharge at these springs appears to come from a fairly large area of alluvial and intermediate groundwater underlying Pueblo Canyon and perhaps part of Los Alamos Canyon. The perchlorate concentration in these groundwater zones is falling with time.

Reference

Purtymun, W. D., Geologic and hydrologic records of observation wells, test holes, test wells, supply wells, springs, and surface water stations in the Los Alamos area, 339 pp., Los Alamos National Laboratory Report LA-12883-MS, January 1995.