

NEW MEXICO ENVIRONMENT DEPARTMENT

**Chromium Transport in the Regional Aquifer,
Mortandad Canyon, New Mexico**

**DOE Oversight Bureau
1183 Diamond Dr. Suite B, Los Alamos, NM 87544**

Patrick Longmire, Aqueous Geochemist, PhD

July 11, 2013

Table of Contents

Executive Summary	2
1.0 Chromium Distributions in the Regional Aquifer	3
2.0 Natural Attenuation of Contaminants	7
3.0 Groundwater-Flow Rates Based on Carbon-14 Dates.....	8
4.0 Groundwater-Flow Rates, Chromium Adsorption, and the Retardation Factor	11
5.0 Chromium(VI) Transport Rates in the Regional Aquifer.....	13
6.0 Chromium Transport Based on the R-28 Pumping Test	14
7.0 Chromium Transport to the Regional Water Table and Pueblo de San Ildefonso Boundary.....	14
8.0 Summary and Conclusions	17
9.0 References	19

List of Figures

Figure 1.	Chromium(VI) Concentrations in the Regional Aquifer, Los Alamos National Laboratory, New Mexico	4
Figure 2a.	Dissolved Chromium Concentrations Measured at R-42, Mortandad Canyon, New Mexico	5
Figure 2b.	Dissolved Chromium Concentrations Measured at R-28, Mortandad Canyon, New Mexico	5
Figure 2c.	Dissolved Chromium Concentrations Measured at R-50 Screen 1, Mortandad Canyon, New Mexico	6
Figure 2d.	Dissolved Chromium Concentrations Measured at R-43 Screen 1, Mortandad Canyon, New Mexico	6
Figure 3.	Groundwater-Flow Rates in the Regional Aquifer Based on Carbon-14 Dates, Los Alamos National Laboratory, New Mexico ...	10
Figure 4.	Groundwater Flow and Chromium Transport Rates in the Regional Aquifer Based on R-28 Pumping Test Results	16

Executive Summary

The purpose of this communication is to constrain contaminant-flow rates for chromium(VI) [Cr(VI)] in the regional aquifer beneath Mortandad Canyon, New Mexico. Dissolved concentrations of anthropogenic (man-made) Cr typically range from greater than 6 µg/L up to 1250 µg/L in the regional aquifer beneath Sandia and Mortandad canyons. The New Mexico Water Quality Control Commission (WQCC) groundwater standard for total dissolved Cr is 50 µg/L (0.050 mg/L) and the US EPA drinking water standard for total Cr (non-filtered) is 100 µg/L (0.10 mg/L). Monitoring well R-50, located 358 feet north of the Pueblo de San Ildefonso boundary, contains increasing concentrations of total dissolved Cr approaching 100 µg/L. R-50 is located hydraulically upgradient from the Pueblo de San Ildefonso boundary and offsite migration of Cr(VI) needs to be evaluated by drilling a monitoring well 600 to 1200 feet south-southeast of R-50. Several approaches are used to quantify groundwater-flow rates and bound Cr transport times, including unadjusted carbon-14 dates of groundwater, pumping test results conducted at monitoring well R-28, and concentrations of Cr measured at several monitoring wells.

Chromium(VI) is stable as CrO_4^{2-} (chromate) under circumneutral pH conditions (6.5 – 8.5) and does not significantly adsorb onto ferric (oxy)hydroxide and clay minerals under moderately oxidizing and basic pH conditions characteristic of the regional aquifer (Puye Formation and Miocene Pumiceous Unit). Chromate mobility is considered to be nearly equal to that of the average linear groundwater-flow rate within the regional aquifer under oxidizing and basic pH conditions, based on site-specific experimental and field investigations conducted by LANL (2012) and NMED. Calculations quantifying Cr transport times using site-specific hydrological and geochemical data are presented in this report. Results of the groundwater-flow and first-order transport calculations suggest that Cr-contaminated groundwater reached the Pueblo de San Ildefonso boundary between 1996 and 2000 with an earlier first arrival transport time being more likely.

Three options are available for evaluating further actions or pathways regarding significant Cr(VI) contamination in the regional aquifer at LANL. These options include:

No Action at this Time

The DOE Oversight Bureau (OB) recommends that if DOE takes no action at this time, the agency should proactively engage with Pueblo de San Ildefonso and NMED regulators to discuss a path forward. In light of this recommendation, the OB interprets, that the Cr(VI) plume(s) has already encroached upon Pueblo de San Ildefonso property based on geochemical and hydrological data presented in this report.

Continued Monitored Natural Attenuation (MNA)

The DOE OB recommends a two-tier approach for this alternative.

1. Groundwater geochemical data show increasing concentration trends of Cr over time at several monitoring wells— Discuss a path forward with NMED regulators.

2. Groundwater geochemical data show decreasing concentration trends over time.
 - Continue periodic monitoring to assure MNA is the correct remedy. At this time, the DOE OB interprets, however, that Cr(VI) concentrations are increasing over time based on extensive monitoring data presented in this report.

Preferred Alternative

The OB recommends that DOE continue characterization and bounding of the Cr(VI) plume(s) through placement of one or more monitoring wells at the inferred edges of the contaminant front or boundary. The OB strongly recommends that a single-screen monitoring well be drilled 600 to 1200 feet south-southeast of R-50, based on the high mobility of Cr(VI) in the regional aquifer (Puye Formation and Miocene pumiceous sediments) beneath Mortandad Canyon and geochemical and hydrological data presented in this report and provided by LANL (2012).

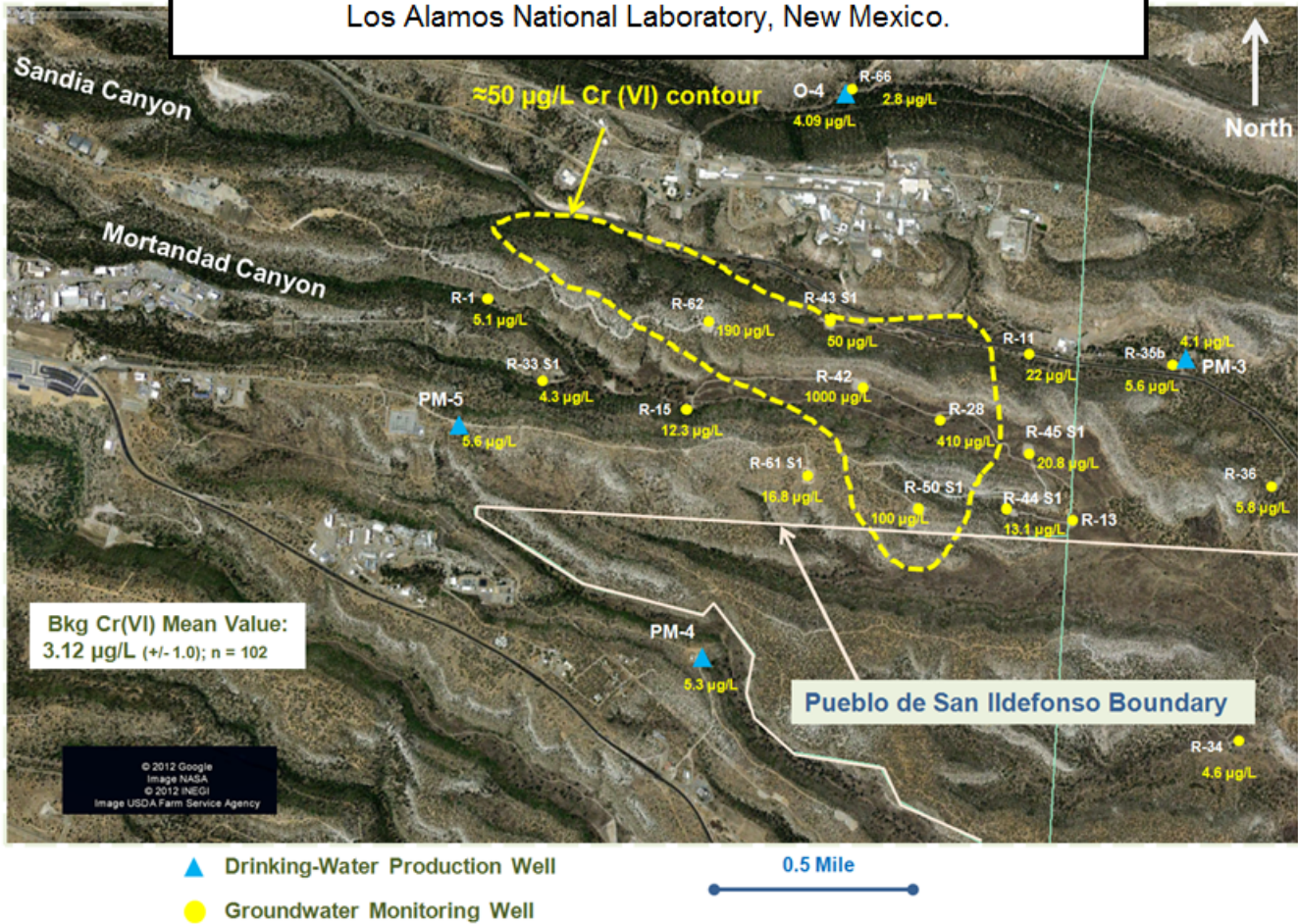
1.0 Chromium Distributions in the Regional Aquifer

Figure 1 shows total dissolved Cr [Cr(III, VI)] concentrations measured in groundwater samples collected from numerous monitoring wells completed in the regional aquifer. The highest dissolved Cr concentrations are measured at monitoring wells R-42 and R-28, which represent the centroid of the Cr plume(s). The dashed line shown in Figure 1 represents an inferred Cr isopleth at 50 µg/L, which extends south of monitoring well R-50. The New Mexico Water Quality Control Commission (WQCC) groundwater standard for total dissolved Cr is 50 µg/L (0.050 mg/L) and the US EPA drinking water standard for total (non-filtered) Cr is 100 µg/L (0.10 mg/L). Locations of several regional aquifer supply wells, including O-4, PM-1, PM-3, PM-4, and PM-5, with total dissolved Cr concentrations are also shown in Figure 1. The mean background concentration of total dissolved Cr is 3.12 ± 1.0 µg/L in the regional aquifer, based on 102 groundwater samples analyzed for the New Mexico Environment Department (NMED) by ALS Laboratories (<http://www.alsglobal.com>) using high resolution mass spectrometry (HRMS). Concentrations of total dissolved Cr in the NMED background data set are above analytical detection and reporting limits.

The Cr plume is oriented in a northwest to southeast configuration, 20 degrees south of east (LANL, 2012), west of R-42, with a more southerly geometry (65 degrees south of east (LANL, 2012), occurring between monitoring wells R-42, R-28, and R-50 (Figure 1). The occurrence of high permeability zones trending in a northwest-southeast direction within the Puye Formation and the Miocene pumiceous unit near R-28 (LANL, 2012) may control the direction of groundwater flow and Cr migration toward R-50 in the upper saturated portions of the regional aquifer. The Cr plume is advancing at the location of R-50, characterized by increasing concentrations of this contaminant over time. Other LANL-derived contaminants, including tritium (^3H), nitrate (NO_3^-), perchlorate (ClO_4^-), 1,4-dioxane, nickel (Ni), chloride (Cl^-), chlorate (ClO_3^-), and sulfate (SO_4^{2-}) occur within the regional aquifer beneath Mortandad Canyon at concentrations above background, but below NMED and USEPA groundwater-drinking water standards. These contaminants are soluble and mobile in regional aquifer groundwater.

Chromium Transport in the Regional Aquifer, Mortandad Canyon, New Mexico

Figure 1. Chromium(VI) Concentrations in the Regional Aquifer, Los Alamos National Laboratory, New Mexico.



Figures 2a, 2b, 2c, and 2d show time versus total dissolved Cr concentrations measured in groundwater samples collected at monitoring wells R-42, R-28, R-50 Screen 1, and R-43 Screen 1, respectively. Increasing concentrations of Cr are observed to a varying degree at R-42, R-43 Screen 1, and R-50 Screen 1, which suggests that the Cr plume(s) is expanding and that, possibly this contaminant is reaching the regional water table at multiple locations beneath Sandia and Mortandad canyons. Rates of increase of Cr concentrations vary at these three wells, with R-43 Screen 1 and R-50 Screen 1 showing more defined and uniform higher slopes relative to initial Cr concentrations measured during sampling. Groundwater mixing is occurring between Cr-contaminated and non-contaminated regional aquifer groundwater, which results in dilution of Cr along groundwater-flow paths. Variations in anthropogenic Cr concentrations have been observed at the monitoring wells over several years, which may reflect limited adsorption/desorption of Cr(VI) with regional aquifer sediments near and in contact with fluctuating water-table elevations. This variation may also result from a heterogeneous flux of Cr entering the regional aquifer system. Regional-aquifer groundwater is strongly oxidizing, having measureable concentrations of dissolved oxygen (4 – 7 mg/L) and concentrations of dissolved iron (0.020 mg/L) and manganese (0.001 mg/L) less than analytical detection. The aqueous geochemistry and mineralogy of the regional aquifer maintains stability of Cr(VI).

Figure 2a. Dissolved Chromium Concentrations Measured at R-42, Mortandad Canyon, New Mexico (source of data - LANL)

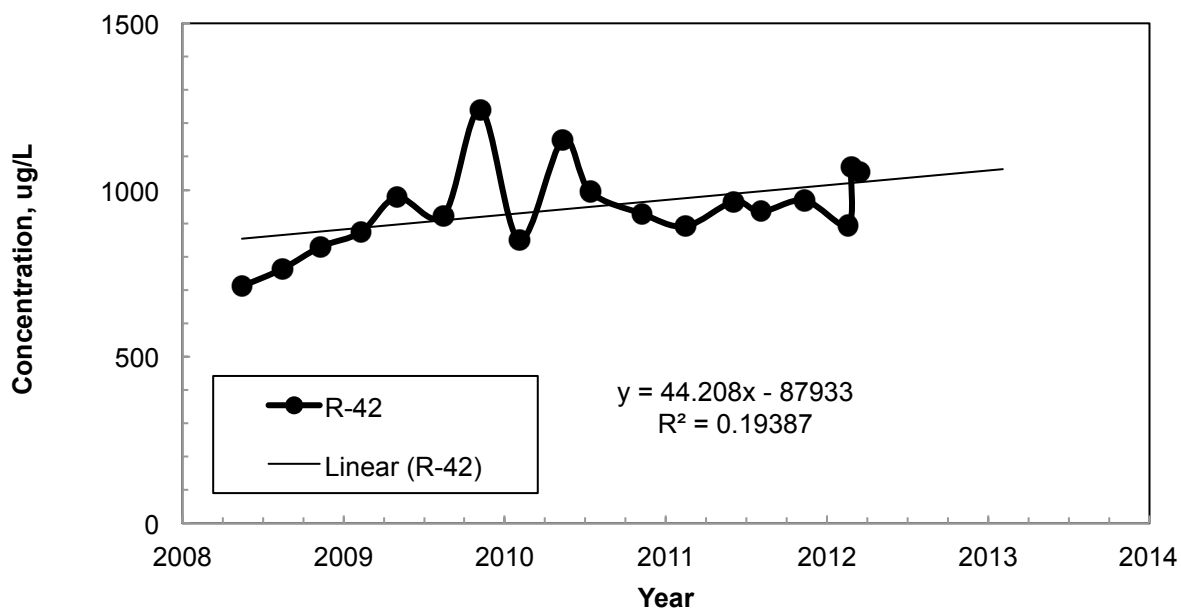


Figure 2b. Dissolved Chromium Concentrations Measured at R-28, Mortandad Canyon, New Mexico (source of data - LANL)

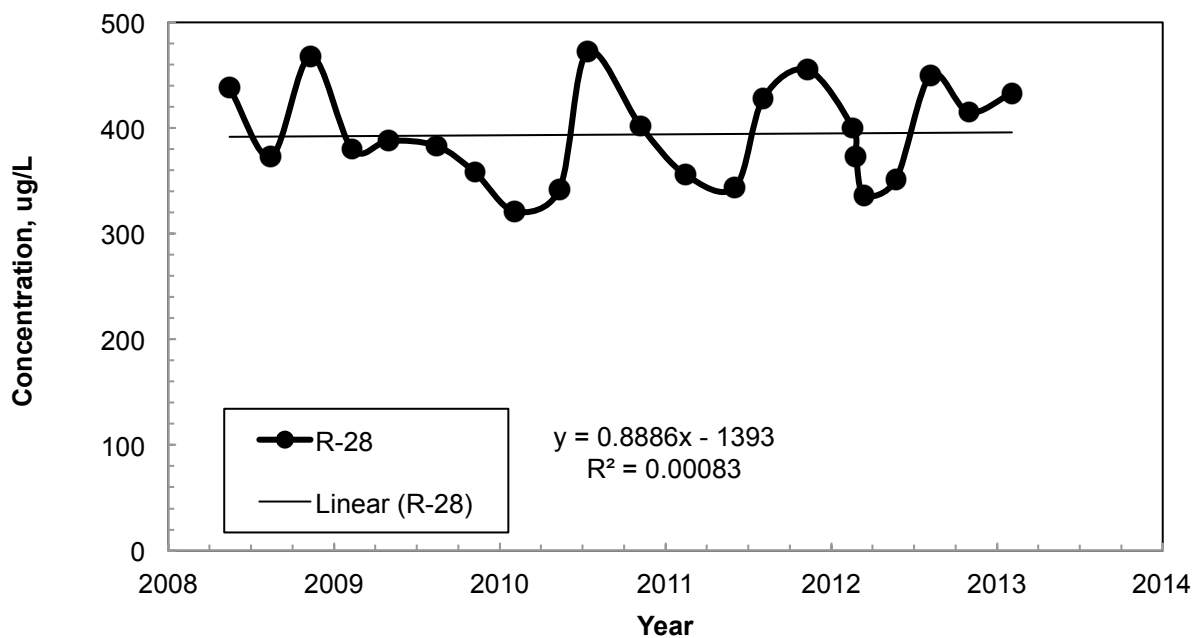


Figure 2c. Dissolved Chromium Concentrations Measured at R-50 Screen 1, Mortandad Canyon, New Mexico (source of data - LANL)

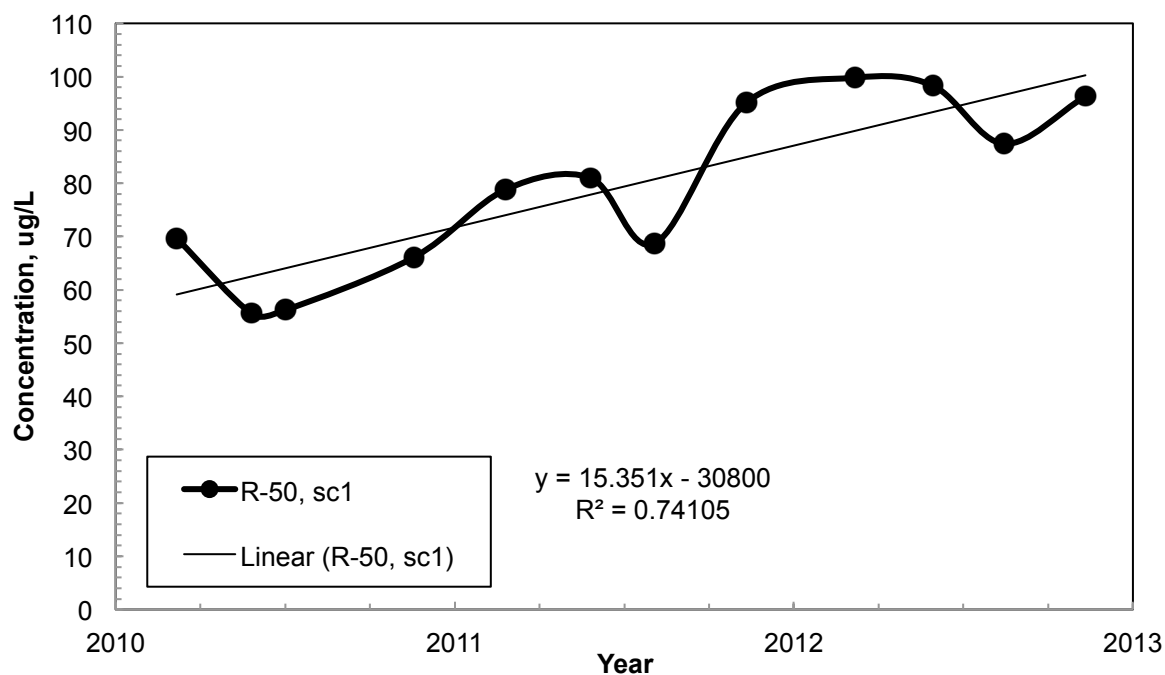
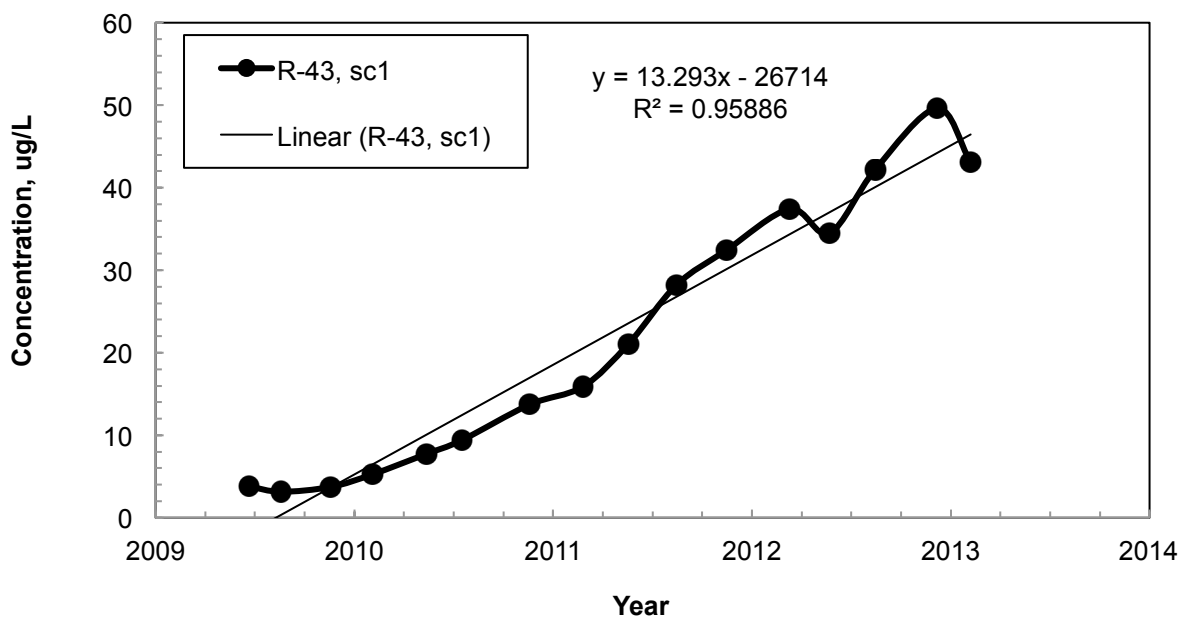


Figure 2d. Dissolved Chromium Concentrations Measured at R-43 Screen 1, Sandia Canyon, New Mexico (source of data - LANL)



Correlation coefficients (R^2) for time versus increasing Cr concentrations at R-42, R-43 Screen 1 and R-50 Screen 1 are 0.194 (Figure 2a), 0.959 (Figure 2d), and 0.741 (Figure 2c), respectively. This is reflective of the high mobility of CrO_4^{2-} under moderately oxidizing and basic pH conditions characteristic of the regional aquifer. Chromium concentrations at R-42 show a pronounced increase between 2008 and 2010 and remain steady afterwards (Figure 2a). The highest overall linear slope of 44.21 is at R-42 because this well contains the highest Cr concentrations. The correlation coefficient, however, is very low and the slope is not uniform with a steep increase occurring from 2008 to 2010 followed by steady state and a slight decrease in Cr concentrations from 2010 to 2012. Chromium concentrations observed at R-28 illustrate steady-state conditions as shown in Figure 2b with an R^2 value of 0.001 for Cr concentrations observed at R-28. Groundwater dilution and dispersion are the dominant physical processes leading to decreasing Cr concentrations between R-42 and R-28, with R-42 most likely located near the major entry point to the regional aquifer.

2.0 Natural Attenuation of Contaminants

Natural attenuation of contaminants occurs in groundwater systems under site-specific conditions, and is dependent on the type and solubility of the contaminant, groundwater chemistry, redox chemistry of aquifer matrix, mineralogy, contaminant flux and concentration, groundwater-flow rate, dispersion, and contaminant- and groundwater-residence times. Natural attenuation of an inorganic or organic contaminant in groundwater systems is supported by:

1. Decreasing concentrations of the contaminant over time,
2. Decreasing volume of contaminated aquifer material over time,
3. Presence of organic intermediate compounds,
4. An abundance of reactive electron donors (reducing agents) , required especially for Cr(VI) reduction, and electron acceptors (oxidizing agents)
5. An abundance of strong adsorption sites present on mineral surfaces to allow for irreversible or weak desorption,
6. Rapid kinetics enhancing mineral precipitation with slow dissolution rates,
7. A sufficiently long groundwater-residence time to allow for biodegradation, adsorption, and precipitation processes to take place within a reasonable time frame, and
8. Achieving contaminant concentrations at or below regulatory standards within a reasonable time frame.

Based on extensive monitoring data and characterization studies conducted by LANL (LANL, 2009 and 2012) and NMED, natural attenuation of Cr(VI) is not taking place to a significant extent at R-42, R-28, R-43 Screen 1, R-50, R-62, and at other monitoring wells showing either increasing or steady-state above-background concentrations of this soluble oxyanion. Geochemical field data (LANL, 2012, NMED data) confirm that the regional aquifer (Puye Formation and Miocene pumiceous sediments) is too oxidizing to enhance precipitation of amorphous $\text{Cr}(\text{OH})_3$. Concentrations of total dissolved iron (Fe) and manganese (Mn) are commonly less than 20 and 3 $\mu\text{g/L}$, respectively, in groundwater samples collected from monitoring wells, which is consistent with moderate to strongly oxidizing groundwater conditions that maintain Cr(VI) stability. Dissolved Fe is stable dominantly as Fe(III) hydrolysis species in the regional aquifer, based on results of speciation modeling using the computer code PHREEQC (Longmire, unpublished data). Geochemical calculations using PHREEQC suggest that dissolved Cr concentrations in equilibrium with reactive amorphous $\text{Cr}(\text{OH})_3$ are less than 5 $\mu\text{g/L}$, which is consistent with background Cr concentrations measured in the regional aquifer, but not for Cr-contaminated groundwater.

Increasing concentrations of Cr(VI) measured during numerous sampling events at various monitoring wells strongly suggest that natural attenuation of this redox-sensitive metal is not taking place to a significant extent. It is unlikely that natural attenuation would ever result in Cr(VI) concentrations less than 50 $\mu\text{g/L}$ at R-28, R-42, and R-50. Natural attenuation of Cr(VI) in the regional aquifer (Puye Formation and Miocene pumiceous sediments) is strongly suppressed by:

1. Insufficient concentrations of electron donors or reducing agents such as magnetite, metal sulfide phases including pyrite, and solid organic matter;
2. Stability of strongly oxidizing groundwater conditions in the presence of dissolved oxygen, manganese(IV), and iron(III);
3. High aqueous solubility of metal-Cr(VI) phases; and,
4. A low adsorption capacity of regional aquifer sediments for Cr(VI) under basic pH conditions.

3.0 Groundwater Flow Rates Based on 14-Carbon Dates

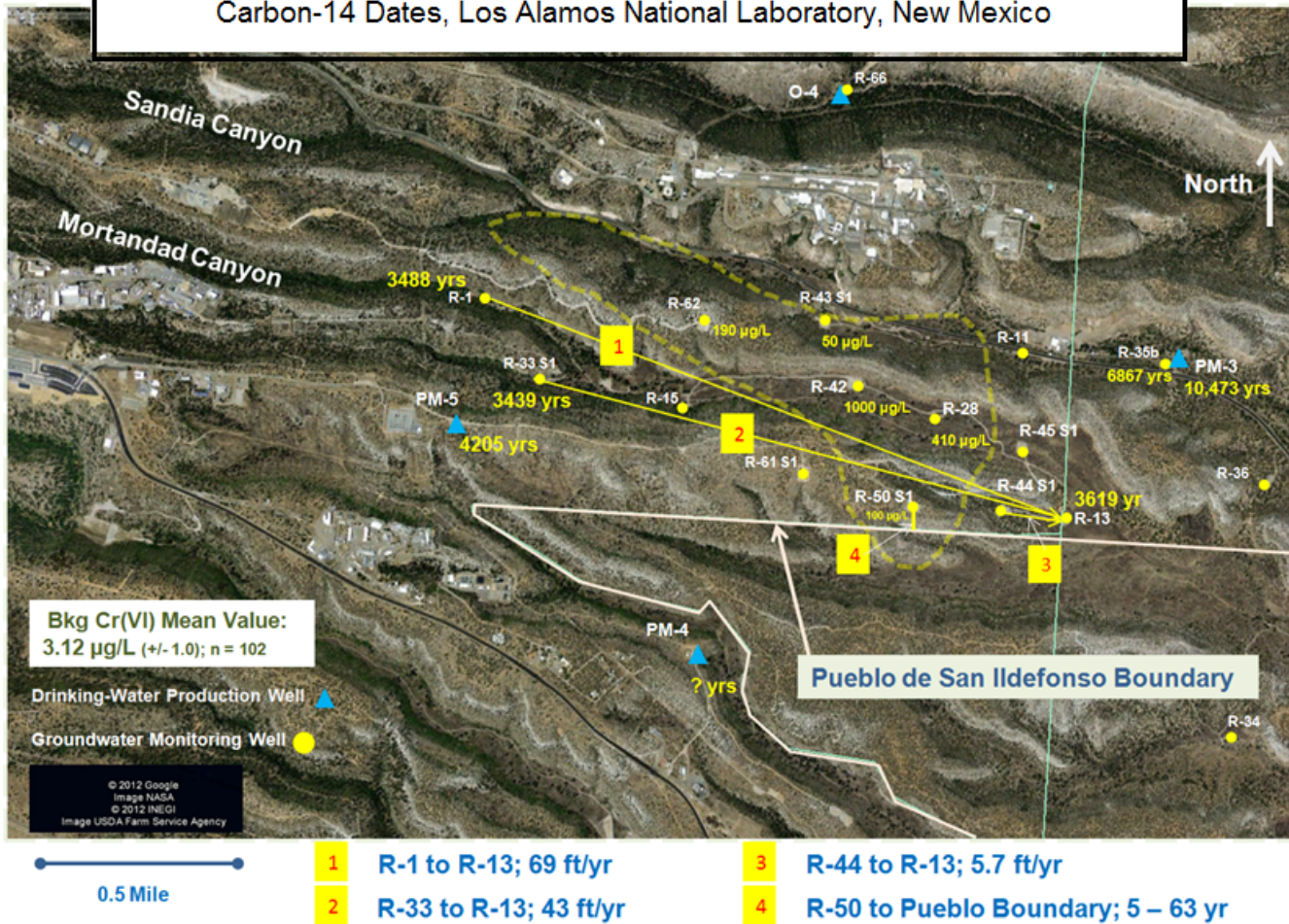
Figure 3 shows a map of unadjusted carbon-14 dates measured in groundwater samples collected from regional aquifer wells located in Mortandad Canyon. Unadjusted carbon-14 dates are used to estimate groundwater-flow rates between several background wells (R-1, R-13, R-33 Screen 1, and R-44 Screen 2) drilled in Mortandad Canyon. These selected monitoring wells are located along groundwater-flow paths with elevations of the regional water table decreasing to the east (LANL, 2012). The above wells selected for carbon-14 dating have not experienced appreciable recharge since the early 1940s and represent background conditions within the regional aquifer, based on extensive monitoring data collected by the NMED and LANL. Mortandad Canyon did not receive significant recharge prior to 1943 when the

Laboratory was established. The head of Mortandad Canyon is located on the Pajarito Plateau, which limits the surface area for infiltration to take place prior to Laboratory discharges. Dissolved concentrations of Cl, Cr, NO_3^- , ClO_4^- , bicarbonate (HCO_3^-), and other solutes are within background distributions at the above wells (LANL, 2012, NMED data). Groundwater samples collected from the wells have activities of low-level tritium less than analytical detection (0.28 pCi/L, University of Miami), also suggesting that recent recharge has not taken place. Recharge containing constituents derived from the Cerro Grande fire of May 2000, mainly consisting of elevated concentrations of TDS, potassium (K), calcium (Ca), TOC, HCO_3^- , and other solutes, has not reached the regional water table at background well locations beneath Mortandad and Sandia canyons. This observation is based on extensive monitoring data collected by LANL and NMED since 2000.

Estimated groundwater-flow rates determined from unadjusted carbon-14 ages, however, are not entirely reliable because analytical errors (1 sigma) associated with carbon-14 measurements are close to the differences in average groundwater ages, especially for R-13 and R-44 Screen 2. Unadjusted carbon-14 ages of groundwater beneath Mortandad Canyon, however, increase along the dominant groundwater-flow direction generally from a westerly to easterly direction, which has been established by LANL (2009, 2012). Groundwater-flow vectors shown in Figure 3 are in reasonable agreement with potentiometric contours (approximately 90 degree orientation with respect to potentiometric contour for isotropic and homogenous aquifer material) determined by LANL (LANL, 2012). Groundwater flow-rates in the regional aquifer are considered to be relatively fast beneath Mortandad Canyon, based on aquifer performance testing conducted at R-28 and the narrow range of unadjusted carbon-14 dates obtained from groundwater samples collected and analyzed from the background monitoring wells.

Chromium Transport in the Regional Aquifer, Mortandad Canyon, New Mexico

Figure 3. Groundwater-Flow Rates in the Regional Aquifer Based on Carbon-14 Dates, Los Alamos National Laboratory, New Mexico



Based on unadjusted carbon-14 age differences between R-1 and R-13, R-33 Screen 1 and R-13, and R-44 Screen 2 and R-13, the following groundwater flow-rates are provided in the absence of recent recharge.

- From R-1 to R-13, with a distance of 9029 feet and an age difference of 131 years, the calculated flow rate is 0.19 feet/day or 69 feet/year.
- From R-33 Screen 1 to R-13, with a distance of 7744 feet and an age difference of 180 years, the calculated flow rate is 0.12 feet/day or 43 feet/year.
- From R-44 Screen 2 to R-13, with a distance of 963 feet and an age difference of 170 years, the calculated flow rate is 0.02 feet/day or 5.7 feet/year.

Calculated groundwater-flow rates, based on unadjusted carbon-14 age differences, range from 5.7 feet/year to 69 feet/year in the regional aquifer beneath Mortandad Canyon. Groundwater-flow rates estimated from unadjusted carbon-14 dates, however,

are biased low compared to those determined from aquifer performance testing conducted at R-28 in 2004 and 2012 (LANL, 2012).

4.0 Groundwater-Flow Rate, Chromium Adsorption, and the Retardation Factor

An average linear groundwater-flow rate for the regional aquifer beneath Mortandad Canyon is calculated from data provided by LANL (2012), based on a pumping or aquifer performance test conducted at R-28 in 2012. Using an assumed effective porosity (n_e) of 0.30, a hydraulic gradient (dh/dl) of 0.0015 feet/feet calculated from differences in water level measurements between monitoring wells R-42 and R-28 and potentiometric maps provided by LANL (2012), and a hydraulic conductivity (K) of 40 feet/day based on the 2012 R-28 pumping test results (LANL, 2012), the average linear groundwater-flow rate (V) (Freeze and Cherry, 1979) is:

$$V = (K)(dh/dl)(1/n_e)$$

$$0.20 \text{ feet/day or } 73 \text{ feet/year} = (40 \text{ feet/day})(0.0015 \text{ feet/feet})(1/0.30)$$

This value represents a lower bound for a groundwater-flow rate for the regional aquifer at R-28. Kleinfelder (2005) report hydraulic conductivities of 140 to 160 feet/day estimated from a 24-hour pumping test conducted in 2004, which results in average linear groundwater-flow rates ranging from 256 and 292 feet/year, respectively. LANL (2012) states that groundwater-flow rates at R-28, based on aquifer performance testing conducted in 2012, may range from 131 to 164 feet/year or higher.

Oxidation-reduction chemistry controls aqueous speciation, adsorption, and precipitation of Cr(III, VI), which influences its geochemical properties and rate of transport in groundwater systems. Chromium(VI) has the potential to weakly adsorb onto ferric (oxy)hydroxide coatings present in the Puye Formation and the Miocene Pumiceous Unit; however, most of Cr(VI) is dissolved based on extensive groundwater monitoring data collected by LANL and NMED. Concentrations of Cr measured in filtered and nonfiltered groundwater samples range from 300 to 1250 $\mu\text{g/L}$ at R-28 and R-42 since 2004 (LANL, 2012, NMED data).

Adsorption or distribution coefficients (K_d), which quantify removal or adsorption of dissolved Cr onto solid aquifer material (adsorbate), were measured by LANL (2009). The K_d values range from 0.1 to 2 mL/g, using non-crushed cutting material collected from R-35b completed in the Puye Formation. The R-35b cutting samples best represent hydrogeologic conditions encountered at R-50 located in Mortandad Canyon approximately 360 feet north of the LANL-Pueblo de San Ildefonso boundary. The samples were not crushed or ground and particle sizes ranged from 500 to 2000 μm (0.5 to 2.0 mm). These samples most closely represent natural or undisturbed material, and coarse-grained particles have the lowest surface area and provide the least amount of Cr(VI) adsorption. LANL (2009) report higher K_d values associated with fine-grained and crushed and ground samples collected from the Puye Formation, which typically do not represent natural conditions and fast groundwater-flow paths in the regional aquifer.

It is very likely that many of the adsorption sites present on hydrous ferric oxide, smectite, and other adsorbents are saturated with Cr(VI) and maximum attenuation of Cr has already been established, and this process appears to be not significant in terms of mass removal from regional aquifer groundwater.

The retardation factor (Freeze and Cherry 1979), R_f quantifies Cr(VI) adsorption and rate of contaminant movement by the following equation:

$$R_f = 1 + K_d(p/n_e),$$

where K_d is the linear distribution coefficient (mL/g or cm³/g), p is the bulk density (g/cm³), and n_e is the effective porosity (v/v).

Mobile solutes such as chloride, nitrate, or bromide have R_f values equal to unity with a K_d value equal to zero. Strongly adsorbing solutes such as lead or cesium have higher K_d values (>50 mL/g) and are generally not mobile in groundwater under circumneutral pH conditions. Higher R_f values for adsorbates are associated with immobile chemicals such as lead and cesium in aquifer systems.

Measured K_d values for Cr adsorbing onto coarse-grain Puye Formation sediments range from 0.1 to 2 mL/g (LANL, 2009). It is likely that more adsorption of Cr(VI), however, takes place on fine-grain adsorbents, such as ferric (oxy)hydroxide and smectite, characterized by larger surface areas, present in the Puye Formation. In addition to limited adsorption of Cr(VI) in the regional aquifer, reduction of Cr(VI) to Cr(III) provides an effective process for removing Cr from groundwater under specific hydrochemical conditions in the presence of iron(II) in pristine or fresh magnetite (Fe₃O₄ or Fe(III)₂Fe(II)O₄). Presence of reactive magnetite in the Puye Formation and Miocene Pumiceous Unit can provide a limited reduction capacity resulting in the precipitation of amorphous or crystalline Cr(OH)₃. Groundwater chemical data and Cr stable isotope data (LANL, 2012, Appendix H), however, show that the reduction capacities of the Puye Formation and Miocene pumiceous sediments are very limited. The estimated bulk density and effective porosity for the Puye Formation are 1.5 g/cm³ and 0.30, respectively.

Lower Bound for R_f (least amount of Cr adsorption)

$$R_f = 1 + (0.1 \text{ mL/g})(1.5 \text{ g/cm}^3)/(0.30) = 1.5.$$

Average linear groundwater-flow rates in the Puye Formation and the Miocene pumiceous sediments are 1.5 times faster than Cr(VI) transport rates based on an R_f of 1.5.

Upper Bound for R_f (higher amount of Cr Adsorption)

$$R_f = 1 + (2 \text{ mL/g})(1.5 \text{ g/cm}^3)/(0.30) = 11.0.$$

Average linear groundwater-flow rates in the Puye Formation and the Miocene pumiceous sediments are estimated to be 11 times faster than Cr(VI) transport rates based on an R_f of 11. This range of R_f values suggests that regional aquifer groundwater migrates 1.5 to 11 times faster than Cr(VI) under advective groundwater-flow conditions. The lower R_f value of 1.5 suggests higher mobility of Cr(VI) in Puye Formation and the Miocene pumiceous sediments, which is considered more representative of Cr(VI) distributions in the regional aquifer beneath Mortandad Canyon. Increasing concentration trends of Cr are observed at several monitoring wells, including R-43 Screen 1 and R-50 (LANL, 2012, NMED data), suggesting that the adsorption capacity of regional aquifer sediments is exhausted at these two well locations. The same conditions most likely apply at monitoring wells R-42, R-28, and R-62.

5.0 Cr(VI) Transport Rates in the Regional Aquifer

The bounding estimated transport rates for Cr(VI) under advective groundwater flow-conditions are calculated by:

Cr(VI) transport rate = groundwater-flow rate (feet/year)/ R_f .

The bounding estimated first-order transport times for Cr(VI) (initial appearance) under advective groundwater-flow conditions are calculated by:

Cr(VI) transport time = distance (feet) between wells A and B/Cr(VI) transport rate (feet/year).

First-order calculations presented in this report are used for quantifying Cr transport times under advective groundwater-flow conditions without considering dispersion. This analysis represents the time of first appearance of the contaminant at a given monitoring well. They do not, however, represent contaminant breakthrough at wells defined as $C/C^0 = 0.50$ (Freeze and Cherry, 1979), where C and C^0 are contaminant concentration as a function of time and initial contaminant concentration, respectively. The calculated Cr transport times for advective groundwater-flow conditions represent the lowest contaminant concentrations initially observed at a monitoring well. Increasing concentrations of total dissolved Cr are clearly observed at monitoring wells R-43 Screen 1 and R-50 Screen 1, indicating that contaminant breakthrough is occurring after initial appearance of Cr at these two locations.

Incorporating dispersion coefficients in the first-order calculations described in this paper should result in shorter Cr transport rates and times within the regional aquifer, based on studies reported in the literature. This, however, was not conducted, as dispersion coefficients have not been measured *in situ* for the regional aquifer. Advective transport times for Cr that do not include dispersion represent the longest periods of time for first appearance at a given downgradient monitoring well.

6.0 Chromium Migration Based on the 2012 R-28 Pumping Test

A 10-day aquifer performance or pumping test was conducted at R-28 in 2012 and aquifer parameters are provided by LANL (2012, Appendix L). Groundwater-flow rates ranging from 131 to 164 feet/year were determined from the pumping test.

Groundwater-flow rates and Cr transport rates based on the 2012 R-28 pumping test are presented below.

Cr migration rate = groundwater-flow rate (feet/year)/ R_f .

- (131 feet/year)/1.5 = 87.3 feet/year (upper bound based on a lower R_f and lower groundwater-flow rate);
- (131 feet/year)/11 = 11.9 feet/year (lower bound based on a higher R_f and lower groundwater-flow rate);
- (164 feet/year)/1.5 = 109 feet/year (upper bound based on a lower R_f and higher groundwater-flow rate); and,
- (164 feet/year)/11 = 14.9 feet/year (lower bound based on a higher R_f and higher groundwater-flow rate).

The most representative Cr transport rates most likely range from 87 to 109 feet/year in the regional aquifer at R-28. This is based on extensive monitoring data provided by LANL (2012) and NMED and Cr trend analysis presented above for several wells.

An estimated lower bound of Cr transport between monitoring well R-50 and Pueblo de San Ildefonso boundary is calculated by considering the slowest groundwater-flow rate and highest calculated R_f value presented above. The estimated amount of time for Cr to migrate from R-50 to the Pueblo de San Ildefonso boundary is:

$$358 \text{ feet}/11.9 \text{ feet/year} = 30.1 \text{ years.}$$

An estimated upper bound of Cr transport between monitoring well R-50 and Pueblo de San Ildefonso boundary is calculated by considering the fastest groundwater-flow rate and lowest calculated R_f value presented above. The estimated amount of time for Cr to migrate from R-50 to the Pueblo de San Ildefonso boundary is:

$$358 \text{ feet}/109 \text{ feet/year} = 3.3 \text{ years.}$$

7.0 Chromium Transport to the Regional Water Table and Pueblo de San Ildefonso Boundary

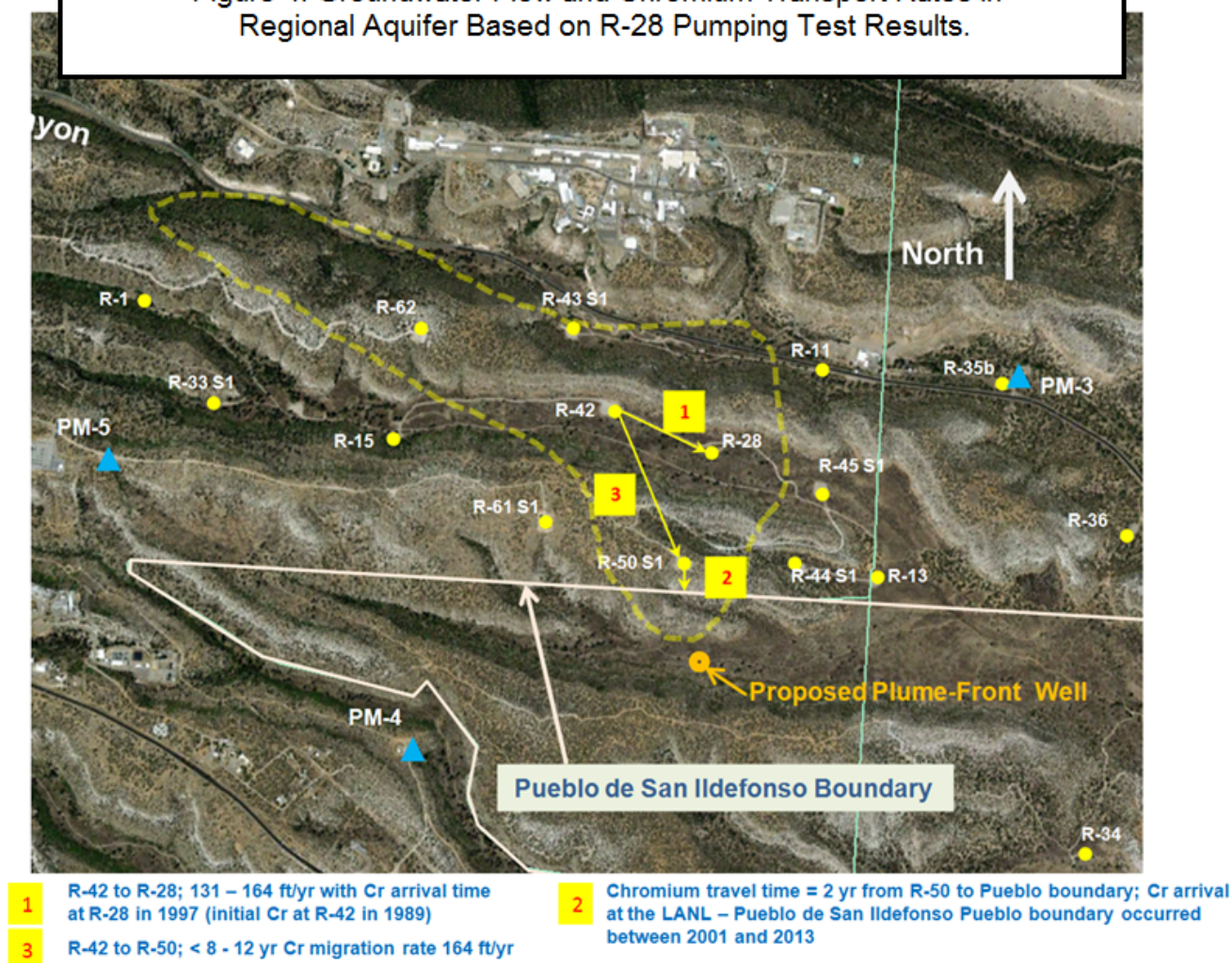
This section provides another independent approach for estimating the initial time of contaminant arrival at the regional water table near R-42, which is useful in evaluating

Cr transport rates in the regional aquifer and initial arrival times at monitoring wells. This analysis is based on results of tritium/helium-3 dating of regional aquifer groundwater at LANL (Longmire et al., 2007). Tritium was initially released from TA-50 to Mortandad Canyon in 1963. In 2005, groundwater samples were collected from R-15 and dated using the tritium/helium-3 method. Results of the radioisotopic measurements taken in 2005 show that tritium has been present in the regional aquifer at R-15 for 16 years (Longmire et al., 2007). This suggests that it took 26 years for tritium to migrate through the vadose zone to reach R-15 in 1989, with initial tritium releases to Mortandad Canyon starting in 1963. Loss of tritium through vaporization in the unsaturated zone, however, may have increased the apparent age of groundwater at R-15 using the tritium-helium dating method. This potentially results in longer apparent transport times for tritium compared to Cr(VI) migrating through the vadose zone beneath Sandia Canyon. Transport of Cr(VI) to the regional water table beneath Sandia Canyon most likely has taken less than tritium transport beneath Mortandad Canyon, which means less than 26 years with a calculated arrival time for Cr near R-42 occurring prior to 1982. Chromium was initially discharged from the Technical Area(TA)-03 cooling tower in 1956 (LANL, 2009). This constraint is based on a higher flux or larger volumes of saturated flow occurring in the vadose zone beneath Sandia Canyon, resulting from long-term releases of treated sewage effluent and cooling tower water since the early 1950s from TA-03. LANL (2012, Appendix J) estimates that the largest contaminant mass of Cr reached the regional water table between 1956 and 2004 with 1980 representing a mid time of arrival. This value agrees very well with the arrival of Cr in 1982 based on tritium/helium dating of groundwater samples collected from R-15.

Figure 4 shows inferred groundwater-flow paths with calculated Cr-transport rates between monitoring wells R-42 and R-28, R-42 and R-50, and from R-50 to the LANL-Pueblo de San Ildefonso boundary. It is likely that Cr initially entered the regional water table near R-42 and then migrated in an easterly direction to R-28 and in a southeasterly direction to R-50 due to anisotropic conditions occurring within the Puye Formation and Miocene pumiceous sediments (LANL, 2012). Anisotropic conditions produce a significant deviation in the direction of groundwater flow with respect to the potentiometric surface of the regional aquifer east and southeast of R-42 (LANL, 2012). Heterogeneity in permeability or hydraulic conductivity of the aquifer sediments within buried paleochannel deposits occurring in the Puye Formation and alluvial fans in the Miocene pumiceous sediments enhance fast groundwater-flow paths. Monitoring wells located downgradient from R-42 and R-28 contain varying concentrations of Cr(VI), suggesting that there are one or more groundwater-flow paths, with differing permeability or hydraulic conductivities, influencing Cr(VI) migration within the Puye Formation and Miocene pumiceous sediments.

LANL (2012) states that the Cr(VI) transport time from R-42 to R-28 may have been less than 8 years (Appendix J), which includes any adsorption of Cr(VI) onto regional aquifer sediments. The distance between the two monitoring wells is approximately 1,312 feet with a calculated minimum Cr(VI) transport rate of 164 feet/year in the Puye Formation and Miocene pumiceous sediments. Transport times for Cr(VI) are estimated between R-42 and R-50 and from R-50 south to the Pueblo de San Ildefonso boundary

Figure 4. Groundwater Flow and Chromium Transport Rates in Regional Aquifer Based on R-28 Pumping Test Results.



using two different groundwater-flow rates including 164 feet/year and 131 feet/year, including any Cr(VI) adsorption onto regional aquifer sediments. The estimates are based on groundwater-flow rates between R-42 and R-28, discussed by LANL (2012), and calculated retardation factors for Cr presented in Section 4.0. The distance between monitoring wells R-42 and R-50 is 1,950 feet. The shortest Cr(VI) transport time for initial arrival at R-50 is estimated at 12 years, assuming that this non-adsorbing solute is migrating at a rate of 164 feet/year (LANL, 2012). Anthropogenic Cr(VI) may have initially reached R-50 in 1994, assuming that Cr arrived at the regional water table near R-42 in 1982. A minimum transport time from R-50 to the Pueblo de San Ildefonso boundary is 2.2 years for the initial appearance of Cr(VI) occurring in 1996. This assumes that the estimated Cr(VI) transport rate of 164 feet/year between R-42 and R-28 is applicable to R-50.

Chromium(VI) migrating at a rate of 131 feet/year (LANL, 2012) from R-42 requires approximately 15 years before initially arriving at R-50 in 1997 and at the Pueblo de San Ildefonso boundary in 2000. The two bounding transport calculations presented above suggest that Cr-contaminated groundwater initially reached the Pueblo de San Ildefonso boundary between 1996 and 2000 with an earlier travel time being more likely. Based on groundwater chemical data collected from R-50 and relatively fast transport rates for

Cr(VI) within the Puye Formation, drilling a single-screen monitoring well 600 to 1200 feet south-southeast of R-50 is strongly recommended.

8.0 Summary and Conclusions

Concentrations of Cr(VI) measured in the regional aquifer exceed both the EPA drinking water standard of 100 $\mu\text{g/L}$ (0.10 mg/L) and New Mexico WQCC groundwater of 50 $\mu\text{g/L}$ (0.050 mg/L) at several monitor wells (R-28, R-42, R-50 Screen 1, and R-62) located in Mortandad Canyon. Concentrations of total dissolved Cr [mainly stable as Cr(VI)] up to 1,250 $\mu\text{g/L}$ have been measured at monitoring well R-42, located in the centroid of the Cr plume(s). The mean background concentration of total dissolved Cr in the regional aquifer is 3.12 ± 1.0 $\mu\text{g/L}$, based on 102 groundwater samples analyzed for the NMED by ALS Laboratories using HRMS.

Natural attenuation of Cr(VI) is not occurring to a significant extent in the regional aquifer beneath Sandia and Mortandad canyons, based on both field and experimental investigations conducted by LANL (2009, 2012) and the NMED. The reduction capacity of the regional aquifer sediments is not substantial based on higher abundance of Fe(III)-bearing silicates and (oxy)hydroxides over Fe(II) phases. The adsorption capacity of the sediments is exhausted within the Cr(VI) plume with concentrations of total and dissolved Cr measured up to 1250 $\mu\text{g/L}$. Increasing or steady-state concentrations of Cr(VI) are observed at several monitoring wells completed in the regional aquifer (Puye Formation and Miocene pumiceous sediments). Regional-aquifer groundwater is strongly oxidizing, having measureable concentrations of dissolved oxygen (4 – 7 mg/L) and dissolved concentrations of Fe (0.020 mg/L) and Mn (0.001 mg/L) less than analytical detection. The reduction capacity of the Puye Formation and the Miocene pumiceous sediments is minimal in the absence of electron donors including iron sulfides, solid organic matter, and dissolved sulfide and methane. Chromium(VI) is highly mobile in the regional aquifer with transport rates nearly identical to that of groundwater-flow velocities within the Puye Formation and the Miocene pumiceous sediments beneath Mortandad Canyon.

The range of calculated transport times for Cr(VI), under advective groundwater-flow conditions, are estimated from monitoring well R-50 to the Pueblo de San Ildefonso boundary:

- 30.1 years based on the 2012 R-28 pumping test with highest R_f for Cr(VI);
- 3.1 years based on the 2012 R-28 pumping test and lowest R_f for Cr(VI).

Based on the first-order Cr transport analysis presented above, the most realistic transport times for Cr(VI) between monitoring well R-50 and the Pueblo de San Ildefonso boundary probably are less than 10 years. Additional geochemical and monitoring data collected by LANL and NMED that support this finding include:

1. Increasing Cr(VI) concentrations observed at R-50 Screen 1 and

2. High Cr(VI) mobility in the Puye Formation and Miocene pumiceous sediments.

Results of the Cr transport calculations presented in this report suggest that Cr(VI)-contaminated groundwater may have reached the Pueblo de San Ildefonso boundary between 2001 and 2007, with an earlier transport time being more likely. A single-screen monitor well drilled 600 to 1200 feet south-southeast of R-50 is strongly recommended.

9.0 References

Freeze, R. A. and Cherry, J. A., 1979, Groundwater. New York, Prentice Hall, 604 p.

Kleinfelder, 2005, Revision 1, Well R-28 Completion Report, report prepared for Los Alamos National Laboratory, Project No. 37151/16.12, Albuquerque, New Mexico.

Longmire et al., 2005, Radiogenic and Stable Isotope and Hydrogeochemical Investigation of Groundwater, Pajarito Plateau and Surrounding Areas, New Mexico, Los Alamos National Laboratory Report LA-14333, 68 p. plus appendices.

Los Alamos National Laboratory, 2012, Phase II Investigation Report for Sandia Canyon, LA-UR-12-24593, September 2012, EP2012-0195, various pagination.

Los Alamos National Laboratory, 2009, Investigation Report for Sandia Canyon, LA-UR-09-6450, October 2009, EP2009-0516, various pagination.

Acknowledgment: "This material is based upon work supported by the Department of Energy Office of Environmental Management under Award Number *DE-EM0002420*."

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."