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# **Phase III RFI Report for Solid Waste Management Unit 16-021(c)-99**

**Volume 1**

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Produced by

Risk Reduction and Environmental Stewardship Division–Remediation Services

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#### **EXECUTIVE SUMMARY**

This document describes results of the Phase III Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) that was conducted at consolidated Solid Waste Management Unit (SWMU) 16-021(c)-99, which is located at Technical Area 16 (TA-16) within the Los Alamos National Laboratory (the Laboratory or LANL). This SWMU is associated with an outfall situated behind a high explosives (HE) processing building (Building 260). The outfall is also known as the TA-16-260 outfall, or the 260 outfall (see Figure 1.2-3). The Phase III RFI, which was conducted from 1999 to 2002, is an integral part of the corrective measures study (CMS) plan and the CMS plan addendum. Sampling was conducted according to the sampling and analysis plan (SAP) included in the CMS plan for SWMU 16-021(c)-99. The plan was approved by the New Mexico Environment Department (NMED) in September 1999. The regulatory status of SWMU 16-021(c)-99 is shown in Table ES-1.

The CMS plan divides the evaluation of transport pathways and the selection of remedial alternatives into an alluvial groundwater CMS and a regional groundwater CMS. The alluvial groundwater CMS is focusing on the Cañon de Valle source area, alluvial groundwater system, and the subsurface tuff and saturated system, including canyon springs. The regional groundwater CMS for SWMU 16-021(c)-99 is a separate investigation into the extent of contamination in the deep perched zone and the regional aquifer. One important goal of the Phase III RFI was to investigate, and incorporate into the conceptual model, the hydrogeologic and contaminant transport dynamics of the Cañon de Valle and Martin Springs alluvial and subsurface groundwater systems. The Phase III RFI data have reduced data uncertainties such as contaminant concentration and distribution for the CMS process.

The following Phase III RFI activities were conducted in support of the alluvial groundwater CMS:

- characterizing the subsurface and alluvial groundwater through the installation of seven piezometers in Cañon de Valle and three alluvial groundwater wells in Martin Spring Canyon;
- determining contaminant dynamics and contamination distribution by sampling alluvial groundwater, surface water, and springs in Cañon de Valle and Martin Spring Canyon;
- determining contaminant inventory and distribution in sediment through geomorphic-based sediment sampling in both Cañon de Valle and Martin Spring Canyon;
- characterizing hydraulic interconnectivity and the residence time of water in the subsurface through a continuing bromide tracer study which was initiated in 1997 and through a stable isotope study;
- characterizing the nature and extent of contamination in the mesa vadose zone through the sampling and analysis of the intermediate-depth perched aquifer;
- identifying potential subsurface contaminant migration pathways using geophysical studies; and
- performing a baseline human health risk assessment for the Cañon de Valle source area and alluvial area [including a comparison of chemical of potential concern (COPC) concentrations for Martin Spring Canyon] and a baseline ecological risk assessment for Cañon de Valle.

#### **SWMU 16-021(c)-99 Source Area**

The SWMU 16-021(c)-99 source area is comprised of a settling pond and an upper and lower drainage channel that extends from the 260 outfall downgradient to the confluence of the drainage and Cañon de Valle. The source area was excavated during an interim measure (IM) conducted from winter 2000

through summer of 2001. The IM removed more than 1300 yd $^3$  of contaminated soil, sediment, and tuff containing approximately 90% of the HE compounds that existed in the source area. HE compounds and barium COPCs still remain in the SWMU 16-021(c)-99 source area in isolated locations throughout the drainage channel. Remaining sources of contamination are associated with either historic HE releases elsewhere in TA-16 or secondary sources such as sediment.

#### **Cañon de Valle Alluvial System Investigation**

The primary COPCs for Cañon de Valle surface water are RDX (cyclotrimethylene-trinitramine) and barium, both of which were detected in surface water samples at the confluence of Cañon de Valle and Water Canyon (approximately 3 mi downstream from the source area). This indicates that the entire Cañon de Valle alluvial system contains RDX and barium. RDX concentrations in the surface water of Cañon de Valle are highest near the 260 outfall area. The highest mass flow rate of RDX in surface water occurred during wet periods.

The primary COPCs for Cañon de Valle alluvial groundwater are RDX, barium, and manganese. There is a positive correlation between saturated thickness in Cañon de Valle alluvial wells and RDX concentration, indicating that RDX residing within the vadose zone constitutes an important secondary source which is released to the alluvial groundwater during high surface water flow events with the corresponding increased saturated thickness in the alluvium. Barium concentration trends in alluvial groundwater over time are stable to slightly decreasing, with spikes associated with pulses of barium into the system, possibly due to sediment flushing.

The primary COPCs for Cañon de Valle sediment are RDX, HMX (cyclotetramethylene-tetranitramine), amino-2,6-dinitrotoluene[4-], amino-4,6-dinitrotoluene[2-], TNT (trinitrotoluene[2,4,6-]), antimony, barium, cobalt, copper, lead, nickel, and silver. The active channel sediment resampling in 2002 (conducted after the Cerro Grande fire in 2000) showed a reduction in RDX and barium in the upper canyon since the 1996 sampling, indicating a contaminant inventory shift. This was probably a result of increased post-fire surface water runoff.

#### **Martin Spring Canyon Alluvial System Investigation**

The COPCs for Martin Spring Canyon surface water are RDX, barium, boron, and manganese. The COPCs for alluvial groundwater include RDX, arsenic, barium, beryllium, boron, cadmium, lead, and manganese. The COPCs in Martin Spring Canyon alluvium, sediment, and tuff include amino-2,6 dinitrotoluene[4-], amino-4-6-dinitrotoluene[2-], RDX, TNT, arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, and silver. Both barium and RDX are present in Martin Spring Canyon sediment, but at much lower concentrations and with much smaller inventories than in Cañon de Valle.

#### **Subsurface Systems—Intermediate-Depth Perched Aquifer and Springs Investigation**

The subsurface system investigations included physical and chemical characterization of SWSC, Burning Ground, and Martin Springs; the 90s Line Pond; and samples collected from five intermediate-depth perched aquifer wells. The springs are a manifestation of the intermediate-depth perched groundwater, present primarily in tuff discontinuities such as fractures and surge beds that underlie the northwestern portion of TA-16. The 90s Line Pond, located on the mesa top, was included because it may be a groundwater recharge source. The springs investigation included quarterly sampling of the three springs and additional flow-integrated samples. Analytical data from these sampling campaigns indicate all three springs contain RDX and TNT as primary COPCs. Intermediate-depth perched groundwater is ephemeral in most of the well locations. Analysis of the intermediate-depth groundwater indicates low levels of contamination. Groundwater wells are frequently dry but, when wet, contaminant levels are detected for

several constituents, including HE compounds. Concentrations exceed contaminant-screening limits for RDX and metals including aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, and zinc.

#### **Conceptual Model**

In general, the conceptual model that was presented in the Phase II RFI still applies on a site-wide basis. The Phase III RFI conceptual model changes have largely been refinements that have reduced data uncertainties for the CMS process.

The key components of the conceptual site model include

- the source area:
- a mesa vadose zone, consisting of nonfractured and fractured tuff and intermediate-depth ephemeral perched groundwater;
- canyon alluvial sediment;
- canyon springs;
- canyon surface water;
- canyon alluvial groundwater;
- a deep vadose zone, consisting of nonfractured and fractured tuff that extends from the canyon bottom to the top of the regional aquifer; and
- the regional aquifer, as defined by the installation of Regional Aquifer Well R-25. While the regional aquifer is not included in the scope of this Phase III RFI, key results from the installation and sampling of Regional Aquifer Well R-25 are important for a general understanding of the conceptual model.

Isotopic differences in composition between mesa vadose zone groundwater and Cañon de Valle alluvial groundwater indicate mesa groundwater probably comes from local precipitation and snowmelt on the mesa top, whereas Cañon de Valle groundwater is at least partially derived from spring flow recharged at higher elevations. Borehole sampling in the mesa vadose zone indicates no contamination in the unsaturated depth intervals in any boreholes except in the immediate vicinity of the former settling pond. These results indicate mesa vadose zone contamination is concentrated beneath source area SWMUs such as the former and current ponds and drainages (90s Line Pond, V-Site Pond, 30s Line Pond) on the mesa top. However, ephemeral groundwater in mesa vadose zone wells not located in the vicinity of the former settling pond have shown contamination, indicating lateral movement (possibly through surge beds) of water and contaminants in the mesa subsurface. In addition, based on the oxygen and deuterium stable isotope results, mesa vadose zone groundwater from Well 16-02665 (Martin Spring Canyon) and Well 16-02669 (90s Line Pond) and surface water from the 90s Line Pond all show evaporative signatures, but spring water does not. These results reinforce the presence of a mesa vadose zone groundwater flow regime that is dominated by fractures and surge beds and, in general, the importance of hydrologic heterogeneity at TA-16.

#### **Human Health Risk—SWMU 16-021(c)-99 Source Area**

The baseline risk assessment for the source area used the list of identified COPCs and evaluated potential exposures to an on-site environmental worker, a trail user, and a construction worker. The onsite environmental worker is assumed to be involved in environmental monitoring such as field sampling efforts. The trail user is a worker using the trails for recreation or exercise such as walking or jogging. The construction worker is assumed to be involved in intrusive work activities such as excavation. Thus, the frequency and duration of exposure differs, though the exposure pathways for all these human receptors are assumed to be the same.

The cumulative excess cancer risk to all human receptors from potential exposures to all COPCs in soil and tuff was slighly above, or less than, the  $1\times10^{-5}$  target risk specified by NMED under both central tendency estimate (CTE) and reasonable maximum exposure (RME) assumptions (cancer risk ranges from  $4\times10^{-7}$  to  $3\times10^{-5}$ ). Noncancer hazards are below, or slightly above, a hazard index (HI) of 1.0 for CTE and RME assumptions (HIs range from 0.2 to 2.0).

#### **Human Health Risk—Cañon de Valle Alluvial Area**

For the Cañon de Valle alluvial area, a trail-user scenario was assessed. Cumulative excess cancer risk to the trail user from potential exposures to all COPCs in sediment and surface water is below the  $1\times10^{-5}$ target risk specified by NMED for CTE and RME assumptions. Noncancer hazards are below an HI of 1.0 for both exposure assumptions.

#### **Human Health Risk**—**Martin Spring Canyon**

A comparison of COPC concentrations was done for Martin Spring Canyon, comparing relative COPC concentrations (maximum and mean) in sediment and surface water to those found at the Cañon de Valle alluvial area. It was concluded that the Martin Spring Canyon COPC concentrations were less than, or within the range of, those found at the Cañon de Valle alluvial area, which has been determined to not pose a potential unacceptable risk to human receptors under the trail-user scenario.

#### **Ecological Risk**—**Cañon de Valle**

For the ecological risk assessment, the process followed US Environmental Protection Agency and NMED guidance. The ecological risk assessment for the terrestrial system in Cañon de Valle found elevated metals concentrations in small mammals but not at levels that are likely to cause adverse effects for the Mexican spotted owl. The numbers of species, population densities, and reproductive classes for those species indicated that the Cañon de Valle small mammal community is not being adversely affected by contaminants.

The ecological assessment of the aquatic system in the canyon found some differences between benthic macro-invertebrates in Cañon de Valle and reference canyons, though these results were not replicated in a subsequent toxicity test, indicating high variability in the contaminant signatures for this sediment. The toxicity testing for Cañon de Valle shows potential impacts relative to the reference site in Starmer's Gulch, although the sediment is heterogeneous with regard to potential toxic effects. In Cañon de Valle, a viable benthic macro-invertebrate community is present, which is a meaningful indicator that site contaminants cause negligible ecological effects.

#### **Conclusions**

- Although the volume of the residual soil within the former outfall source area is less than 100  $yd^3$ (based on field observations), the soil contains elevated concentrations of HE and barium that could be mobilized by stormwater runoff.
- The potential risk for residual contamination in the former outfall source area soil is marginally above NMED's target risk levels for RME for the environmental worker (cancer risk) and the

construction worker (noncancer hazard) and may be within EPA's target risk range; potential risks for CTE exposures and other RMEs for the receptors were below these NMED target levels.

- Sediments in Cañon de Valle and Martin Spring Canyon represent a widely dispersed secondary source for HE and barium that is potentially mobilized by surface water and alluvial groundwater. Moreover, the perennial reach of Cañon de Valle alluvial groundwater provides a high potential for subsequent infiltration of mobilized contaminants.
- The drought has influenced the hydrogeology of the area by reducing mesa vadose zone groundwater recharge, reducing canyon alluvium saturated thickness, and causing SWSC and Martin Spring to dry up.
- Contaminant transport in the mesa vadose zone is dominated by a fracture or surge bed flow regime, of which contaminated springs are a known manifestation. With the IM source removal, a substantial source for this contamination is gone, though reductions in spring contaminant concentrations are not yet evident. More wells are planned in both the mesa vadose zone groundwater and the regional aquifer to further assess the importance of these pathways.
- Cañon de Valle and Martin Spring Canyon surface water, groundwater, springs, and sediment do not pose a potential unacceptable human health risk to the trail user (i.e., potential risks and hazards are below  $10^{-5}$  and HI of 1.0 for all exposures).
- The ecological risk assessment conducted in Cañon de Valle found that COPCs have no adverse effects on terrestrial receptors and have negligible adverse effects on aquatic receptors.

<b>SWMU</b> <b>Number</b>	<b>SWMU Description</b>	<b>HSWA</b>	Radionuclide <b>Component</b>	Proposed <b>Action</b>	<b>Rationale for Recommendation</b>
$16-021(c)$	Outfall and drainage channel	Yes	No.	CMS/CMS report	RCRA contamination within acceptable human health risk and ecological risk ranges; isolated areas of contamination exceed acceptable ranges and will be addressed in CMS

**Table ES-1 Summary of Proposed Actions** 

#### **CONTENTS**





## **List of Appendices**



- [Appendix F](/source/orgs/em/er/projects/Current/HEPS/docs/App_F.pdf) Results of Quality Assurance/Quality Control Activities
- [Appendix G](/source/orgs/em/er/projects/Current/HEPS/docs/App_G/App_G.pdf) Analytical Suites and Results
- [Appendix H](/source/orgs/em/er/projects/Current/HEPS/docs/App_H/App_H.pdf) Water and Sediment Screening Results: Charts, Tables, and Data Files
- [Appendix I](/source/orgs/em/er/projects/Current/HEPS/docs/App_I.pdf) Evaluation of Chemical and Physical Data from the SWMU 16-021(c)-99 Source Area, Cañon de Valle, and Martin Spring Canyon
- [Appendix J](/source/orgs/em/er/projects/Current/HEPS/docs/App_J.pdf) Evaluating the Hydrogeochemical Response of Springs Using Singular Spectrum Analysis and Phase-Plane Plots
- [Appendix K](/source/orgs/em/er/projects/Current/HEPS/docs/App_K.pdf) Human Health Risk Assessments for Cañon de Valle and Screening Risk Assessments for Martin Spring Canyon
- [Appendix L](/source/orgs/em/er/projects/Current/HEPS/docs/App_L.pdf) Ecological Risk Assessment for Cañon de Valle
- [Appendix M](/source/orgs/em/er/projects/Current/HEPS/docs/App_M.pdf) Relevant Documents
- [Appendix N](/source/orgs/em/er/projects/Current/HEPS/docs/App_N.pdf) Water Balance Calculation for Cañon de Valle

#### **List of Figures**















### **List of Tables**











#### **1.0 INTRODUCTION**

Los Alamos National Laboratory (LANL or the Laboratory) is a multi-disciplinary research facility owned by the US Department of Energy (DOE) and managed by the University of California. The Laboratory is located in north-central New Mexico, approximately 60 mi northeast of Albuquerque and 20 mi northwest of Santa Fe. The Laboratory site covers approximately 40 mi<sup>2</sup> of the Pajarito Plateau, which consists of a series of fingerlike mesas separated by deep canyons that contain ephemeral and intermittent streams that run from west to east. Mesa tops range in elevation from approximately 6200 ft to 7800 ft. The eastern portion of the plateau stands 300 to 900 ft above the Rio Grande.

The Laboratory's Risk Reduction and Environmental Stewardship–Remediation Services (RRES-RS) project is involved in a national effort by the DOE to clean up facilities that were formerly involved in weapons production. The goal of the RRES-RS project is to ensure that the DOE's past operations do not threaten human or environmental health and safety in and around Los Alamos County, New Mexico.

This document describes the results of a Phase III RCRA facility investigation (RFI) which was conducted at consolidated Solid Waste Management Unit (SWMU) 16-021(c)-99 from 1999 through 2002. This consolidated SWMU, located within Technical Area 16 (TA-16), includes the TA-16-260 outfall and associated drainage. The Phase III investigation is an integral part of the corrective measures study (CMS) plan (LANL 1998, 62413.3) and the CMS plan addendum and its revision (LANL 1999, 64873.3; LANL 2003, 75986.2).

The CMS plan separates the evaluation of transport pathways and the selection of remedial alternatives into an alluvial CMS and regional groundwater CMS.

The alluvial CMS is focused on the Cañon de Valle source area and alluvial system and on the subsurface tuff and saturated system (for example, perched water, SWSC Spring and Burning Ground Spring in Cañon de Valle, and Martin Spring in Martin Spring Canyon). The Phase III investigation was designed to evaluate interactions among these hydrogeologic systems, to characterize contamination transport through the mesa, and to help define the boundaries of the existing plume(s). Results are presented for the TA-16-260 outfall area as well as the associated hydrogeologic systems potentially impacted by its releases.

This report describes the sampling conducted during the Phase III RFI, examines the analytical results collected for this site, describes and revises the physical and contaminant transport conceptual model developed for the site, and presents human health and ecological risk assessments. Sampling was conducted according to the approach described in the sampling and analysis plan (SAP) which was included in "CMS Plan for Potential Release Site 16-021(c)" (LANL1998, 62413.3). The plan, and its associated Phase III SAP, was approved by NMED in September 1999.

The regional groundwater CMS for SWMU 16-021(c)-99 investigates the extent of contamination in the deep perched zone and the regional aquifer. In addition to Regional Aquifer Well R-25, two additional deep wells have been installed: CdV-R-15-3 and CdV-R-37-2. Three intermediate-depth wells are planned for Cañon de Valle in FY 2004. These wells will help meet the objectives of the Phase III RFI and CMS, although they are not part of this Phase III RFI.

#### **1.1 Purpose and Regulatory Context**

The Phase III RFI, including its sampling and analyses, was conducted under the requirements of RCRA and NMHWA. The investigation of SWMU 16-021(c)-99 was performed in accordance with the Hazardous and Solid Waste Amendments (HSWA) of 1984, and it followed the requirements found in Module VIII of

the Laboratory's Hazardous Waste Facility Permit (EPA 1990, 01585). Module VIII was issued to the Laboratory by the US Environmental Protection Agency (EPA) on May 23, 1990, and was approved on May 4, 1994 (DOE 1994, 35328).

The RCRA corrective action program at SWMU 16-021(c)-99 is being implemented in phases. Table 1.1-1 lists the RCRA corrective action program phases and the RCRA-driven actions that have been, or will be, implemented at SWMU 16-021(c)-99.

The purposes of the Phase III RFI are to (1) collect sufficient data to further define the nature and extent of site contamination, and (2) refine the site conceptual model. Specifically, Phase III sampling is designed to assess the interconnectivity between the source area and springs at TA-16, and between the canyon bottom systems and deeper groundwater systems. Phase III sampling was also designed to evaluate the interactions among the springs, surface water, and alluvial groundwater, and the responses of those components of the site hydrogeologic system to precipitation events and flow conditions. Finally, Phase III sampling was designed to assess contaminant storage and redistribution in canyon sediment. Collectively, these lines of investigation were designed to establish the relationships between contaminant concentration variability and migration and the site hydrogeologic system behavior.

The Phase III data also augment data from previous investigations to support the performance of sitespecific risk assessments and to support the CMS. The objective of the risk assessments are to quantify the potential risks, if any, to human and ecological receptors from exposure to site-related contaminants. The CMS provides a preliminary evaluation of technologies used to remediate contamination at the site, remedial alternatives, characterization of contaminant transport (as detailed in the Phase III SAP), and remedial action designs. Remedial actions are then implemented to mitigate any threat to human health and the environment by removing, containing, or treating contaminated media until established target levels are attained.



## **Table 1.1-1 Chronology of RRES-RS Activities at SWMU 16-021(c)-99**



# **Table 1.1-1 (continued)**



#### **Table 1.1-1 (continued)**

#### **1.2 Facility Location and Background**

TA-16 is located in the southwest corner of the Laboratory (Figure 1.2-1). It covers 2410 acres, or 3.8 mi<sup>2</sup>. The land is a portion of that acquired by the Department of Army for the Manhattan Project in 1943. TA-16 is bordered by the Bandelier National Monument along State Highway 4 to the south, and by the Santa Fe National Forest along State Highway 501 to the west. To the north and east, it is bordered by

TA-8, -9, -11, -14, -15, -37, and -49. TA-16 is fenced and posted along State Highway 4. Water Canyon, a 200-ft-deep ravine with steep walls, separates State Highway 4 from active sites at TA-16. Cañon de Valle forms the northern border of TA-16. Security fences surround the production facilities. A complete discussion of the TA-16 environmental setting is presented in Appendix B to this report.

The administrative boundary for the CMS is shown in Figure 1.2-2. The boundary runs along State Highway 501, which coincides with the Pajarito fault, to the west, and follows the basin divides between Water Canyon and Cañon de Valle to the south, as far as Martin Spring Canyon, Pajarito Canyon, and Cañon de Valle to the north. These basin divides converge at the confluence of Cañon de Valle and Water Canyon. This area will be referred to as the Cañon de Valle basin. The areal extent of the study includes all the surface and subsurface terrain within the boundary except (1) individual SWMUs and associated downgradient areas to the edge of Cañon de Valle, and (2) Fishladder Seep and its sub-basin. These potential contaminant sources are being addressed within the scope of other RRES-RS activities.

The administrative boundary is designed to incorporate contaminant sources and the fate and transport mechanisms of the Cañon de Valle basin. The TA-16-260 outfall is considered the major source of contaminants in the basin. Monitoring and data analysis at the basin scale will support decisions about conducting remedial activities at other potential contaminant source locations as well.

## **1.2.1 Facility History and Operations**

TA-16 was established for the purposes of developing explosive formulations, casting and machining explosive charges, and assembling and testing explosive components for the US nuclear weapons program. Almost all the work has been conducted in support of the development, testing, and production of explosive charges for the implosion method. Present-day use of this site is essentially unchanged, although facilities have been upgraded and expanded as explosive and manufacturing technologies have advanced.

The TA-16-260 facility, in operation since 1951, is an HE machining building that processes large quantities of HE. Machine turnings and HE wash water are routed as waste to 13 sumps associated with the building. Historically, discharge from the sumps was routed to the TA-16-260 outfall (also known as the 260 outfall); at one point, discharge was reportedly as high as several million gal. per year (LANL 1994, 76858).

During the late 1970s, the 260 outfall was permitted to operate by the EPA as EPA Outfall No. 05A056 under the Laboratory's National Pollutant Discharge Elimination System (NPDES) permit (EPA 1990, 12454.2). The last NPDES permitting effort for this TA-16-260 outfall occurred in 1994. The NPDESpermitted TA-16-260 outfall was deactivated in November 1996; it was officially removed from the Laboratory's NPDES permit by the EPA in January 1998. This waste stream is currently managed by pumping the sumps and treating the water at the TA-16 HE wastewater plant.



**Figure 1.2-1. Location of TA-16 with respect to Laboratory technical areas and surrounding landholdings; Building 260 is also shown** 



Administrative boundaries for SWMU 16-021(c)-99 CMS gure 1.2-2. Administrative boundaries for SWMU 16-021(c)-99 CMS **Fi** Both the TA-16-260 outfall and the drainage channel from the TA-16-260 outfall are contaminated with HE and barium. The sumps and drainlines of this facility are designated as SWMU 16-003(k), and the TA-16-260 outfall and drainage are designated as SWMU 16-021(c) in Module VIII of the Laboratory's Hazardous Waste Facility Permit (EPA 1990, 01585). Following LANL's SWMU consolidation effort, the two former SWMUs are now collectively referred to as SWMU 16-021(c)-99. Prior to the Phase I and II RFIs at SWMU 16-003(k) and 16-021(c), known contaminants included barium, RDX, TNT (trinitrotoluene), and HMX (cyclotetramethylenetetranitramine). Suspected contaminants included other HE compounds, additional inorganic chemicals, volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and uranium.

#### **1.2.2 SWMU Descriptions**

SWMU 16-021(c)-99 is a Laboratory consolidation of two designated SWMUs: 16-003(k) and 16-021(c).

SWMU 16-003(k) comprises 13 sumps and approximately 1200 ft of associated drainlines or troughs that lead from the HE machining building (TA-16-260) to the TA-16-260 outfall. HE-contaminated water flowed from the sumps into the concrete drainlines and ultimately to the 260 outfall, located approximately 200 ft east of Building 260. Building 260 is located on the north side of TA-16 (Figure 1.2-3). The structure was originally built in 1951; minor modifications were made to the structure at a later date.

SWMU 16-021(c) is comprised of a well-defined upper drainage channel fed directly by the 260 outfall, a former settling pond, and a lower drainage channel leading to Cañon de Valle. The former settling pond, which was removed during the 2000 IM, was approximately 50 ft long, 20 ft wide, and located within the upper drainage channel, approximately 45 ft below the 260 outfall. The upper drainage channel runs approximately 600 ft northeast from the 260 outfall to the bottom of Cañon de Valle. A 15-ft near-vertical cliff is located approximately 400 ft from the 260 outfall and marks the break between the upper and lower drainage channels.

A small settling pond approximately 55 ft long was originally part of SWMU 16-021(c)-99. HEcontaminated water from the 260 outfall entered the settling pond about 40 ft from the outfall. The settling pond and 260 outfall drainage channel are significant sources of the contamination identified in downgradient components of the SWMU 16-021(c)-99 hydrogeologic system. An IM was conducted during 2000 and 2001, and more than 1300 yd<sup>3</sup> of contaminated soil were excavated from the settling pond and channel. Approximately 90% of the HE that existed in the SWMU 16-021(c)-99 source area was removed during the IM (LANL 2002, 73706). The residual contamination in the source area is addressed in this report and through the ongoing CMS.



#### **1.2.3 Adjacent Land Use**

The land adjacent to the 260 outfall site is dedicated to continued Laboratory operations. Other SWMUs located in the vicinity of the 260 outfall are shown in Figure 1.2-4. The SWMUs with the greatest potential influence on the SWMU 16-021(c)-99 investigation are described below.

- Material Disposal Area (MDA) R (SWMU 16-019)—This MDA is located north of the 260 outfall area. MDA R was constructed in the mid-1940s and used as a burning ground and disposal area for waste explosives and possibly other debris. Potential contaminants at this MDA include HE, HE byproducts, and metals (particularly barium). Use of the site was discontinued in the early 1950s. Soil removal and site investigations were conducted at MDA R following the Cerro Grande fire (LANL 2001, 69971.2).
- The burning ground SWMUs [16-010(b,c,d,e,f), 16-010(h)-99, 16-028(a), and 16-016(c)-99]— These SWMUs are located on a level portion of the mesa in the northeast corner of TA-16. The burning ground was constructed in 1951 for HE waste treatment and disposal. Over the years, hundreds of thousands of pounds of HE and HE-contaminated waste material have been burned at this location. The remaining noncombustible material was subsequently either placed in MDA P, north of the burning ground (through 1984), or taken to TA-54 for disposal (1984 to present). A barium nitrate pile was located at the TA-16 burning ground for many years. Site investigations were conducted at several of these SWMUs in 1995 and later (LANL 2003, 76876). Information was also obtained from investigations conducted between 1997 and 2002 at Flash Pad 387 and the consolidated SWMU 16-016(c)-99. Flash Pad 387 underwent clean closure and the sites representing consolidated SWMU 16-016(c)-99 underwent voluntary corrective action (VCA) concurrently with the MDA P clean closure.
- MDA P (SWMU 16-018)—This MDA contained wastes from the synthesis, processing, and testing of HE; residues from the burning of HE-contaminated equipment; and construction debris. HE waste-disposal activities at this site started in the early 1950s and ceased in 1984. The site is located on the south slope of Cañon de Valle. MDA P recently underwent a cleanup under RCRA in which approximately 55,000 yd<sup>3</sup> of soil and debris were removed (LANL 2003, 76876).
- The 90s Line Pond portion of consolidated SWMU 16-008(a)-99 [former SWMU 16-008(a)]—The 90s Line Pond is an inactive unlined settling pond located a few hundred feet west of Building 260. The pond may have received HE, barium, uranium, and organic chemicals from machining operations discharge from TA-16-89, -90, -91, -92, and -93. As recently as 2002, HE solids were observed at the pond area.

All these SWMUs contain (or did contain, prior to closure, as in the case of MDA P) contaminants similar to those found in SWMU 16-021(c)-99, and all drain into Cañon de Valle. Furthermore, the 90s Line Pond contained standing water that may have created a persistent increase in hydraulic head and could have caused the migration of contaminants and contributed to the effects observed in the Cañon de Valle and Martin Spring Canyon alluvial systems.



According to the Laboratory's comprehensive site plan of 2000 and and its 2001 update (LANL 2000, 76100; LANL 2001, 70210), future land use at TA-16 is designated as HE research and development and HE testing. Most areas within TA-16 are active sites for the Engineering Science and Application (ESA) Division of the Laboratory, and construction of new buildings and other facilities in the area is possible.

#### **1.3 Previous Investigations**

Data have been collected for the 260 outfall [SWMU 16-021(c)] since the early 1970s and have indicated substantially elevated HE contamination in the sediment, outfall, and sump water. Levels up to 27 wt % (270,000 ppm) of HMX and RDX had been documented in the area of the former pond. The data showed HE contamination extending from the discharge point to Cañon de Valle (Baytos 1971, 05913; Baytos 1976, 05920). The historical data have been summarized in the Phase I and II RFI reports for SWMUs 16-003(k) and 16-021(c) (LANL 1996, 55077; LANL 1998, 59891).

This section provides a summary of data from the Phase I and II RFIs and the IM. All available data for the site are used in this Phase III RFI report to build a physical site model that supports risk-assessment and CMS activities. Specific issues regarding the use of the different data sets are addressed in the data sections of this report.

#### **1.3.1 Source Area Investigation**

The Phase I RFI primarily consisted of surface sampling within the drainage area. The Phase II RFI included sampling surface and near-surface material within the drainage and sampling 13 boreholes (BHs) drilled to depths between 17 and 115 ft in and near the drainage. The Phase II RFI also included extensive field-screening using immunoassay methods for RDX and TNT as well as laboratory sampling for HE and other chemicals.

Elevated concentrations of HE and barium were reported within the drainage from the surface down to the soil/tuff interface. Soil depths were about 5.5 ft below the ground surface (bgs) in the former settling pond area and drainage (about 40 to 95 ft downstream from the outfall); soil depths were only about 1 ft bgs close to the mesa (300 to 400 ft downstream from the outfall).

Phase I and II surface sampling showed surface contamination did not extend laterally beyond the reasonably well-defined drainage. Concentrations of the major contaminants (barium and HMX, RDX, and TNT) were downgradient within the drainage and decreased rapidly beyond the settling pond, although substantial levels of HMX and barium were present at the base of the colluvial slope in Cañon de Valle.

Subsurface sampling indicated concentrations also decreased rapidly below the soil/tuff interface. However, up to 1000 mg/kg of HE was found in tuff, within the uppermost tuff unit (Unit 4 of the Tshirege Member of the Bandelier Tuff, Qbt 4), beneath the upper part of the drainage and including the former settling pond area. Almost 1 wt% (10,000 ppm) HE was reported in a saturated sample from BH 16-2700 encountered at a depth of about 17 ft beneath the former settling pond (LANL 1998, 59891). The sample was collected from a surge bed within Unit 4 of the Tshirege Member of the Bandelier Tuff. Below the level of this surge bed, HE was observed only sporadically and at much lower concentrations (less than 5 mg/kg). However, thin surge bed deposits were reported in BH 16-06370, drilled into the center of the former settling pond during the IM (see section 1.3.4 of the IM report), at depths of 40 ft and 46 ft bgs, indicating multiple potential transmissive zones at depth (LANL 2002, 73706).

HE and barium were the principal contaminants found at the 260 outfall, although several other metals, including cadmium, chromium, copper, lead, nickel, vanadium, and zinc, were consistently observed above background levels in the drainage. Other organic compounds (SVOCs, VOCs, and PCBs) were

also detected in one to four samples each. Details and results from the Phase I and II RFIs are presented in two RFI reports (LANL 1996, 55077; LANL 1998, 59891).

#### **1.3.2 Alluvial System Investigation**

Sampling in the Cañon de Valle alluvial system included collection of surface and subsurface sediment, three pairs of overbank sediment samples, filtered and unfiltered surface water, and one quarterly round of filtered and unfiltered alluvial groundwater. These samples were collected during three different investigations which took place in 1994, 1996, and 1997/1998, respectively.

Barium was the most abundant inorganic contaminant in sediment. For the surface samples, barium ranged from 6.3 mg/kg to 40,300 mg/kg. Other inorganic chemicals consistently above the background levels included cadmium, chromium, copper, lead, nickel, vanadium, and zinc. Several types of HE were detected: the amino-dinitrotoluenes (A-DNTs), HMX, nitrobenzene, 3-nitrotoluene, RDX, 1,3,5-trinitrobenzene (TNB), and trinitrotoluene (TNT). The two HE compounds highest in abundance and concentration were HMX and RDX. Their maxima were 170 mg/kg and 42 mg/kg, respectively.

Surface water samples and alluvial groundwater samples from the five alluvial wells and Peter Seep were collected in Cañon de Valle. Filtered/unfiltered sample pairs were collected during 1994 and 1997/98; primarily unfiltered samples were collected in 1996. The differences in concentration between the filtered and unfiltered samples are small. The inorganic chemicals identified as chemicals of potential concern (COPCs) in all water were antimony, barium, chromium, lead, manganese, mercury, nickel, vanadium, and zinc. Barium is the most abundant, with concentrations ranging from 99  $\mu$ g/L to 16,000  $\mu$ g/L. As in the sediment, HE appears to be the other major COPC in Cañon de Valle surface water and alluvial groundwater. The HE COPCs identified were A-DNTs, HMX, nitrobenzene, 2-nitrotoluene, RDX, TNB, and TNT. RDX is the HE highest in concentration, with a maximum concentration of 818 µg/L in surface water. All contaminants decrease downgradient from Peter Seep to the confluence with Water Canyon (LANL 1998, 59891).

#### **1.3.3 Subsurface System Investigation**

The intermediate-depth perched aquifer investigation included drilling five wells (91 to 207 ft) at locations likely to intersect the saturated zones at TA-16. The local trend of subunit-subunit contacts is to the north and east. Three of these wells intersected ephemeral perched water. In each case, the water dissipated in less than 1 month. Analysis of this perched water indicated low concentrations (generally ppb) of contamination.

The springs investigation included quarterly sampling of SWSC, Burning Ground, and Martin Springs. Results indicate all three springs are contaminated with RDX and other HE. Several major cations and anions, including calcium, magnesium, sodium, and boron, were detected. Boron is particularly elevated (1800 µg/L) in Martin Spring. Aluminum, iron, barium, phosphate, and nitrate were also elevated. Although low levels (ppb) of VOCs have been detected in all three springs, detections were sporadic and occurred primarily during the quarterly sampling round of June 1997.

Time-series analysis of the springs data indicates extreme variability in the concentration of constituents (up to a factor of 20 in RDX concentration at Martin Spring). Similarities in element variability and flow rate changes over time indicate that SWSC Spring and Burning Ground Spring are hydrogeologically related, but that Martin Spring probably represents a different hydrogeological system.

A potassium bromide tracer was deployed at SWMU 16-021(c) during April 1997. A breakthrough of bromide ions was observed in SWSC Spring during August 1997. Bromide breakthrough may also have occurred at Burning Ground Spring during August 1997, but the effects were more subtle, due to partial masking by variability in all the anions (LANL 1998, 59891). This indicates that the springs are hydrologically connected to the SWMU 16-021(c) source area.

#### **1.3.4 IM at the 260 Outfall**

An IM was conducted from the winter of 2000 through the summer of 2001 to remove contaminated material from the 260 outfall drainage area. It successfully removed the bulk of contamination from the outfall drainage channel. More than 1300 yd $^3$  of contaminated soil were excavated and disposed of at offsite facilities. Of this amount, more than 200 yd<sup>3</sup> of characteristic hazardous waste for reactivity (D003), which contained HE in concentrations of approximately 2 wt% (20,000 ppm), were treated by the selected disposal facility prior to final disposition. An IM report for SWMU 16-021(c)-99, which was completed in 2002, details the activities and results (LANL 2002, 73706).

#### **1.4 Conceptual Understanding and Approach**

TA-16 is a complex site in terms of geohydrologic behavior and contaminant fate and transport, and there are many uncertainties associated with the conceptual model. The most thorough conceptual model going into the Phase III RFI was detailed in the Phase II RFI report (LANL 1998, 59891) and is summarized below.

- Saturated flow systems occur in different forms. These include the alluvial surface water and groundwater in Cañon de Valle; the SWSC, Burning Ground, and Martin Springs; and the 90s Line Pond.
- The saturated systems that feed the springs are hypothesized to be flow through localized fracture zones or surge beds.
- Recharge of the saturated zones may occur via various sources and processes, including the Pajarito fault zone, the steam plant drainage, and the 90s Line Pond.
- Recharge may also occur via transient saturated flow or via matrix or porous media flow.
- The 260 outfall was a primary source of contamination for SWSC Spring and possibly Burning Ground Spring. Contaminants in Martin Spring may have come from a source other than the 260 outfall. Martin Spring chemistry and flow behavior is substantially different from those of the Cañon de Valle springs.

Although the hydrogeological system is better understood and the conceptual model is more clearly defined following the Phase III investigation, many of the same questions that were asked after the Phase II RFI remain.

These questions may be translated into specific data needs. The approach to Phase III data collection was focused on answering these questions and on improving the understanding of the conceptual model. The data collection objectives are summarized in Table 1.4-1 and the sampling plan is detailed in the CMS plan (LANL 1998, 62413.3).

Overall, the approach to the RFI/CMS at the 260 outfall has been tailored to focus on source identification together with the delineation of soil and sediment contamination and confirmation of groundwater and surface water contamination. During this process, the data have been continually evaluated to determine
if contamination is present, if it presents a potential risk to human health or the environment, if it has been sufficiently delineated, and what further action(s) is needed.

Based on current understanding of the site, the conceptual model for the 260 outfall includes a complex set of contaminant transport pathways and hydrogeologic features. Contaminant transport pathways are structurally controlled in the underlying Bandelier Tuff by fractures and other preferential pathways such as surge beds between tuff units. Major uncertainties in the conceptual model result from this complexity, particularly regarding the location of saturated zones in the subsurface and associated contaminant transport pathways at the site. The presence of the saturated zones may also be seasonal or episodic. Further study of the site is warranted to understand the dynamics of contaminant transport and to determine the effects of post-remedial actions. Even as more data are collected at the site, substantial uncertainties may remain in the conceptual model. It is not necessary or feasible to determine the exact extent of contamination at the site in a detailed and spatially explicit manner. Extent can only be described in an overall sense based on current understanding and on monitoring data as they are obtained. Sufficient understanding of the site will be obtained for the purposes of selecting and implementing corrective measures that will mitigate potential risk to human and ecological receptors.

<b>Technical</b> Category	<b>Investigative Questions</b>	<b>RFI Sampling Program</b>	<b>Location in</b> <b>Phase III RFI</b> Report
Hydraulic connectivity	1. How is the 260 outfall connected to TA- 16 springs and seeps?	Potassium bromide tracer inventory-continued sampling of springs and seeps to detect tracer	Section 2.2.2
	2. Are there other transport pathways that connect directly to perched groundwater or regional groundwater?	Perched groundwater intermediate borehole drilling $(5$ BHs)	Section 4.4.2.2
		Regional groundwater drilling (not covered in this report)	Not applicable
Residence times	1. How long does it take water to travel from a recharge point(s) to the TA-16	Precipitation sampling and stable isotope analysis	Section 3.4.2.1.4, Appendix B
	springs and seeps?	Spring/seep sampling for isotopic analysis	Section 4.4.2.2.9, Appendix B
Alluvial water dynamics	1. What is the overall water balance in Cañon de Valle? Does the perennial reach have unidentified losing stretches?	Monitoring surface and subsurface discharge profiles in perennial reach (6 alluvial wells, 15 stream profile locations)	Section 3.4.2.1.4, Appendix H
		Precipitation measurement and sampling	Section 3.4.2.1.4, Appendix B
		Geophysical surveys	Section 3.4.2.1.4, Appendix D
		Calculating overall water balance	Section 5.2.5, Appendix N
	2. What is the nature of the Martin Spring Canyon alluvial water dynamics?	Water sampling and analysis; installed 3 alluvial wells	Section 3.4.2.3 and 3.4.2.4

**Table 1.4-1 Data Objectives for the Phase III RFI as Defined in the SAP** 



### **Table 1.4-1 (continued)**

*Source:* LANL 1998, 62413.3.

To complete the RFI/CMS at this site, activities will continue to be performed in compliance with the following documents:

- A CMS plan (issued in September 1998 [LANL 1998, 59891])—the CMS plan includes a preliminary evaluation of technologies that can be applied to the source area contaminated soil, alluvial sediment, spring water, and surface water; a process and criteria for evaluating remedial alternatives; a Phase III SAP for characterizing contaminant transport through the mesa, to the springs, and to the alluvial system; and a design strategy for long-term monitoring to assess trends in contaminant concentrations and fluxes over time.
- An IM plan (issued in November 1999 [LANL 1999, 64355.4])—this plan details the source removal effort needed to accomplish the IM and considers practical engineering approaches. The plan includes a SAP that characterizes the extent of contamination remaining in the environment following source removal.
- An IM report (issued in September 2002 [LANL 2002, 73706])—the IM was conducted from winter 2000 through summer 2001. The report documents the results of removing contamination from the 260 outfall source area. It details post-remediation characterization and bromide inventory sampling.
- A Phase III RFI report (this report)—this report documents the results of the Phase III data collection, the conceptual model refinement, and the post-IM characterization. The report includes human health as well as ecological site-specific risk assessments, both of which will be used during the CMS.
- An alluvial CMS report (to be issued in November 2003)—this report will focus on the contaminants remaining in the unsaturated subsurface and the alluvial system in Cañon de Valle. The intermediate and regional groundwater CMS report (scheduled to be issued in March 2006) will focus on the extent of contaminants in the deep perched zone and the regional aquifer. Remedial alternatives and long-term monitoring requirements will be addressed in both reports.

Throughout the completion of the CMS at this site, the technical team will continue to work closely with the Groundwater Protection Program and the Canyons Investigations Team to complete data collection activities using compatible and consistent approaches. Following the completion of the CMS for the 260 outfall, the Groundwater Investigations Team and the Canyons Investigations Team will conduct further evaluations of the Cañon de Valle groundwater system.

# **1.5 COPC Screening Methodology for Human Health Risk**

In order to identify which chemicals are COPCs for SWMU 16-021(c)-99, all chemicals detected in either solid media (soil, sediment, or tuff, hereinafter collectively referred to as sediment) or water are subjected to a screening methodology. The screening methodologies for sediment and water are depicted in Figures 1.5-1 and 1.5-2, respectively, and described in this section. The SWMU 16-021(c)-99 screening methodology evaluates COPCs based on the following criteria: (1) detect status and frequency of detection; (2) comparison to Laboratory-wide BVs (LANL, 1998, 09730) for solid media; (3) comparison to state and/or federal promulgated standards for water; and (4) screening action levels (SALs) for sediment, soil, and tuff. Steps 1 through 3 are described within sections 3.0 and 4.0 of this report. Step 4 is described in the risk assessments provided in Appendix K. Chemicals that fail screening are retained as COPCs and are evaluated in one or more subsequent analyses: (1) a statistical analysis for background concentrations (soil, sediment, and tuff), provided in Appendix I-1; (2) a geochemical analysis to determine site-specific naturally occurring concentrations (water only), provided in Appendix I-2; (3) an uncertainty analysis, provided in Appendix K; and (4) risk assessments, provided in Appendix K. This prioritized screening process is consistent with the COPC evaluation methods presented in EPA's Risk Assessment Guidance for Superfund (RAGS) (EPA 1989, 08021).

General chemistry cations/anions and related parameters that are not relevant to human health risk assessment have been eliminated from the screening methodology and are not presented in the frequency-of-detected-chemicals tables or screening tables. Specifically, the eliminated cations/anions and related parameters include alkalinity, ammonia, bromide, chlorate, hardness, iodide, oxalate, phosphorus, orthophosphate (expressed as PO4), silicon dioxide, total organic carbon, and total phosphorus. Additionally, calcium, sodium, magnesium, potassium, and iron are essential nutrients and are eliminated from human health risk assessment.

Because an IM was conducted for the SWMU 16-021(c)-99 source area, two separate data screenings are required for Cañon de Valle: (1) a soil and tuff screening of the 260 outfall source area data to identify any post-IM COPCs that might contribute to potential risk, and (2) a baseline sediment and water screening for Cañon de Valle area data in support of a baseline human health risk assessment for the Cañon de Valle canyon bottom. In addition, data screening was conducted for Martin Spring Canyon sediment and water to support a screening risk assessment.

The frequency of detection and background screening for sediment in the 260 outfall source area was conducted as part of the IM. No new soil and tuff data have been collected in the source area since the IM; hence, no additional screening is required. A summary of the IM screening results is provided in section 2.0 (Table 2.3-1 and Table 2.3-2). However, sediment and water sampling in the Cañon de Valle and Martin Spring Canyon has continued since the Phase II RFI, thus a full screening of post-1998 data is presented in section 3.0, section 4.0, Appendix I-1, and Appendix K. All available data (pre- and post-1998) for sediment and water are evaluated in the risk analyses for Cañon de Valle and Martin Spring Canyon presented in Appendix K.

# **1.5.1 Frequency of Detection**

Both sediment and water data for SWMU 16-021(c)-99 have been initially evaluated based on how frequently a chemical is detected in a particular medium at a site. Evaluating chemicals based on their frequency of detection is important because infrequently detected chemicals may be artifacts in the data due to sampling, analytical, or other problems, and therefore may not be representative of true site conditions or operations (EPA 1989, 08021). Moreover, chemicals that are not detected in any of the samples taken for a particular medium are commonly eliminated from further analysis because there is no indication that the chemicals are present at the site (EPA 1989, 08021).

For SWMU 16-021(c)-99, all chemicals that reported 0% detection in a particular medium (i.e., a medium for which only U- or UJ-qualified data are reported for that chemical) are eliminated as COPCs with no further evaluation. Without detection, there is no indication that these chemicals are of potential concern for human health and/or the environment at SWMU 16-021(c)-99.

In addition, most chemicals that were analyzed for a particular medium in more than 20 samples, but reported or detected in less than 5% of the samples, are also eliminated. Based on RAGS guidance, these chemicals may be considered data sampling artifacts that do not represent the site's true conditions (EPA 1989, 08021). However, it is important to note that not all chemicals reporting less than 5% detection for a particular medium are eliminated: the decision to eliminate infrequently detected chemicals from further COPC evaluation depends on whether adequate detection limits are reported for the chemicals in question. Laboratory analytical methods such as dilution and matrix effects can cause detection limits to become elevated which then introduces a level of uncertainty into the data (see Appendix F). For SWMU 16-021(c)-99 data, the evaluation of adequate detection limits is based on whether they are below a chemical's designated benchmark concentration (e.g., a screening level) or regulatory standard. In samples for which the detection limit exceeds the defined benchmark concentration, the chemical is retained for further evaluation.



**Figure 1.5-1. COPC screening methodology for soil, sediment, and tuff** 



**Figure 1.5-2. COPC screening methodology for water** 

# **1.5.2 Comparison to Laboratory-Wide BVs (Soil, Sediment, and Tuff)**

All detected inorganic chemicals (including radionuclides) in SWMU 16-021(c)-99 solid media are screened against the corresponding Laboratory-wide BVs for soil, sediment, and Bandelier Tuff (LANL 1998, 59730). For each chemical, the maximum reported detected value, as well as the maximum reported detection limit, is compared to the corresponding LANL 95% upper tolerance limit (UTL) or BV. Chemicals reporting all data below the 95% BV UTL are eliminated as COPCs. Chemicals reporting either a detected or an undetected concentration exceeding the BV were retained as COPCs and evaluated further. For SWMU 16-021(c)-99, all detected organic chemicals are retained as COPCs and evaluated further.

# **1.5.3 Comparison to Regulatory Standards (Water Only)**

The Laboratory has not established BVs for chemicals in water; therefore, all detected chemicals in SWMU 16-021(c)-99 water are screened against state and federal promulgated water standards that adhered to the following criteria: (1) they are protective of human health and the environment, and/or (2) they are applicable standards for the site.

Both EPA maximum contaminant levels (MCLs) 40 CFR part 141 and 143 (EPA 2002, 76871) and the following New Mexico Water Quality Control Commission (NMWQCC) regulations numeric standards (20.6.2 and 20.6.4 New Mexico Administrative Code [NMAC]) are identified as standards that meet the above criteria and are representative of the conditions found at SWMU 16-021(c)-99:

- NMWQCC surface water (SW) livestock watering standards (20.6.4.900 NMAC)
- NMWQCC SW wildlife habitat standards (20.6.4.900 NMAC)
- NMWQCC groundwater (GW) human health standards (20.6.2.3103 NMAC)
- NMWQCC GW standards for irrigation use (20.6.2.3103 NMAC)
- NMWQCC GW standards for domestic water supply use (20.6.2.3103 NMAC)

The remaining NMWQCC SW standards for (1) irrigation, (2) domestic water supply (superceded by the EPA MCLs screening), (3) human health, and (4) fisheries are not appropriate standards for SWMU 16-021(c)-99. NMWQCC SW standards for irrigation and domestic water supply do not apply to the water at SWMU 16-021(c)-99 because Cañon de Valle and Martin Spring Canyon surface water is not currently, nor is it likely to be in the foreseeable future, designated for irrigation or domestic water supply purposes (LANL 1998, 62413.3; LANL 2000, 76100; LANL 2001, 70210). SW standards derived for the protection of human health and fisheries are also not applicable to Cañon de Valle and Martin Spring Canyon surface water because the morphology of the stream does not allow water to pool. Therefore no habitat exists to support fish in these systems and human consumption of SW is unreasonable for the canyon systems.

The objective of screening is to identify all COPCs for further evaluation; therefore, the most conservative standard is selected as the screening standard. This conservative approach is most clearly observed in the screening of chemicals for which both a NMWQCC regulations numeric standard and an EPA MCL is available. In this case, the more conservative standard (the lower concentration) is chosen for comparative screening purposes. In the absence of both a NMWQCC regulations numeric standard and an EPA MCL, the corresponding EPA Region 6 tap water preliminary remediation goal (PRG), or a Region 9 PRG if no Region 6 PRG is available, is selected and assigned as the screening limit.

Chemicals for which there is neither a regulatory standard nor a PRG are retained as COPCs and subsequently evaluated in the human health and ecological risk assessments or, if one is available and appropriate, a surrogate chemical is assigned. Using surrogate chemicals provides a more complete screening process. The following criteria are used to select appropriate surrogate chemicals for SWMU 16-021(c)-99 data: structural similarity, isometric form, and impurity and metabolite characteristics. These criteria are outlined in the Laboratory document, "Human Health Risk-Based Screening Methodology" (LANL 2002, 72639). Attachment A to that document provides a short list of chemicals for which LANL has already identified surrogates: these surrogates were adopted and used at SWMU 16-021(c)-99, where applicable. For the additional chemicals found at SWMU 16-021(c)-99 that are not listed in Attachment A, surrogates were selected using the same criteria listed above.

For the screening, either the maximum detected concentration and/or the maximum detection limit for a chemical are evaluated against the screening level. Those chemicals whose maximum detected concentrations exceed the screening standards are retained for further evaluation. Those chemicals for which only the maximum detection limit exceeds the screening level are also retained for further evaluation. Those chemicals for which neither the maximum detected concentration nor the maximum detection limit exceeds the screening level are eliminated as COPCs.

# **1.6 Report Organization**

This report is organized identically to the Phase II RFI report. The report consists of eight sections and fourteen appendixes. To simplify presentation of such a large volume of complex environmental data, a three-compartment approach—as negotiated between the NMED Hazardous Waste Bureau (HWB) and LANL personnel—has been used for this report. Each of the three compartments represents a major investigation within the Phase III data collection activities: (1) the source area investigation, (2) the alluvial system investigation, and (3) the subsurface system investigation.

The source area investigation and its results are presented in section 2.0. Section 3.0 contains the alluvial system investigation and its results. Section 4.0 presents the subsurface investigation and its results. Section 5 discusses the updated understanding of the site conceptual model. Section 6 summarizes the human health risk assessments for the source area and the Cañon de Valle canyon bottom as well as the ecological risk assessment for Cañon de Valle. (The entire human health and ecological risk assessments are presented in Appendixes K and L, respectively.) Section 7 presents the report conclusions. Section 8 is a reference list that includes all of the documents cited in the body and the appendixes of this report. The parenthetical information following each in-text reference provides the author, publication date, and ER ID number. This information can be used to locate cited documents as follows.

The ER ID number is assigned by RRES-RS to track material associated with RRES-RS activities. All cited documents are assigned ER ID numbers. An ER ID number can be used to help the reader locate a copy of the actual document at the Records Processing Facility (RPF) and, where applicable, within the RRES-RS Reference Library. Copies of this reference library are housed at NMED-HWB, DOE, and the RRES-RS Project Office. This library is a living document that was developed to ensure that NMED has all of the necessary material to review the decisions and actions proposed in documents submitted by RRES-RS. The library will be updated to include appropriate documents cited in this report.

The fourteen appendixes to this report provide additional information about the Phase III RFI and are listed in Table 1.6-1.



# **Table 1.6-1 Table of Appendixes**

# **2.0 SOURCE AREA INVESTIGATION**

The SWMU 16-021(c)-99 source area is composed of a settling pond and an upper and lower drainage channel that extends from the 260 outfall downgradient to the confluence with Cañon de Valle. The source area was excavated during an IM conducted from winter 2000 through summer of 2001. The IM removed more than 1300 yd<sup>3</sup> of contaminated soil, sediment, and tuff and approximately 90% of the HE that existed in the source area. Post-removal confirmation sampling was conducted to characterize the residual contamination, and bromide inventory confirmation sampling was conducted to evaluate the mass of bromide tracer in the source area. The IM activities are discussed in detail in the IM report for SWMU 16- 021(c)-99 (LANL 2002, 73706). This section summarizes the post-IM sampling activities and bromide inventory, and expands on the data presentation and data summary presented in the IM report.

## **2.1 IM Data Needs and Objectives**

The overall objective of the IM was to substantially reduce the bulk of the source area contamination, with the intent that it would minimize the potential for contaminant migration (LANL 2002, 73706). Excavation was not intended to remove all contamination or to demonstrate that the IM reached acceptable levels of final cleanup; therefore, final cleanup goals were not established as part of the IM. However, an action criterion of 100 mg/kg for residual RDX concentration was used to guide the excavation.

The objective of the post-IM sampling strategy was to characterize the residual HE and other contaminant concentrations in the surface and near-subsurface in the drainage channel. Sufficient data were collected as part of the IM to support the human health risk assessment as summarized in section 6.0 and detailed in Appendix K of this report. The post-removal characterization data are also used to refine the conceptual model and supplement the CMS data.

The objective of the bromide inventory was to estimate the mass of bromide tracer remaining in and near the source area following the IM. Once the mass of bromide tracer remaining in the source area (where the tracer was applied) is known, as well as the starting mass and the mass of tracer at discharge points, the assumption can be made that the remainder of the tracer remains within (and is migrating in) the subsurface system. This information can clarify the connectivity and transport processes within the complex hydrogeologic system.

# **2.2 Scope of Sampling and Analysis**

The post-removal sampling strategy is discussed in detail in the TA-16-260 IM plan and TA-16-260 IM report (LANL 2000, 64355.4; LANL 2002, 73706) and is summarized below. This section also describes the sampling of the removed source material and subsurface material underlying the settling pond in support of the bromide inventory study.

#### **2.2.1 Field Investigation for Post-Removal Sampling**

Surface and near-surface samples were collected during September 2000, immediately following the primary IM removal activities. The ranked-set sampling (RSS) statistical procedure (Patil et al. 1994, 59113) was used to select the location and number of post-removal screening and fixed-laboratory analysis samples.

Forty-five surface and near-surface samples were collected throughout the source area and upper drainage channel for field-screening for HE compounds using high performance liquid chromatography (HPLC). Based on the HE screening, 15 samples were analyzed at an off-site contract analytical

laboratory for metals, HE, SVOCs, VOCs, and total uranium. Following the IM, isolated areas of RDX concentrations exceeding the 100 mg/kg action criterion were identified from the confirmation sample analyses. Additional soil and tuff removal was conducted at these areas, and five additional confirmation samples were collected during June 2001, after the subsequent removal action. Three of the fifteen original sample locations (16-06379, 16-06390, and 16-06403) were resampled. Two new sample locations were also selected for analysis (16-06378 and 16-06404). The five samples collected during June 2001 were also analyzed for polychlorinated biphenyls (PCBs).

Based upon geology and pre-excavation contaminant levels, the surface and near-surface samples were selected from three distinct strata:

- Stratum A—surface material from the excavated drainage channel between the outfall and the edge of the cliff (includes upper drainage channel and settling pond).
- Stratum B—surface material from the drainage channel between the base of the cliff and the drainage channel confluence with Cañon de Valle (includes lower drainage channel).
- Stratum C—subsurface material from the center of the upper drainage channel between the outfall and the cliff.

Selection of the screening samples from each strata is described below:

- Stratum A—18 screening samples were collected along 6 transects (3 samples per transect) spaced at 65-ft intervals from the outfall to the cliff.
- Stratum B—18 screening samples were collected from 6 transects (3 samples per transect) spaced at 42-ft intervals between the base of the cliff and the drainage channel confluence with Cañon de Valle.
- Stratum C—9 screening samples were collected; 1 screening sample was collected from each of 9 locations spaced at 45-ft intervals along the centerline of the upper drainage channel between the outfall and the cliff.

For Stratum A and Stratum B, each transect was considered a discrete set consisting of three samples units (a sample unit being an individual environmental sample). Each set was randomly numbered and then assigned to one of two groups or "RSS cycles." Each of the two RSS cycles in Stratum A and Stratum B therefore consisted of three sets (three transects) and three observations (environmental samples) each. From the groups of screening samples, six analytical laboratory samples were collected from Stratum A, six were collected from Stratum B, and three were collected from Stratum C, for a total of fifteen off-site fixed analytical laboratory samples.

The post-IM screening sample locations and off-site analytical laboratory sample locations are shown on Figure 2.2-1 and are listed in Table 2.2-1.



**Figure 2.2-1. Post-IM sample locations** 











# **Table 2.2-1 (continued)**

Location ID	<b>Sample Location</b>	Screening Sample ID	<b>HPLC</b> <b>HMX</b> (mg/kg)	<b>HPLC</b> <b>RDX</b> (mg/kg)	<b>HPLC</b> <b>TNT</b> (mg/kg)	<b>Total</b> <b>HE</b> (mg/kg)	<b>Laboratory Sample ID and</b> <b>Sample Selection Basis</b>
16-6414	Stratum B; 131 ft downgradient from cliff, center of drainage.	RE16-00-1345	361	20	1	382	<b>NA</b>
16-6415	Stratum B; 131 ft downgradient from cliff, 10 ft north of drainage center.	RE16-00-1346	295	6	$\mathbf{1}$	302	<b>NA</b>
16-6416	Stratum B; 131 ft downgradient from cliff, 10 ft south of drainage center.	RE16-00-1347	1	U	$\cup$	$\mathbf 1$	Sampled in September 2000, Lowest RDX value in Stratum B cycle 2, set 1
16-6417	Stratum B; 173 ft downgradient of cliff, center of drainage.	RE16-00-1348	$\overline{2}$	3	$\cup$	5	<b>NA</b>
16-6418	Stratum B; 173 ft downgradient from cliff, 10 ft north of drainage center.	RE16-00-1349	U	U	$\cup$	0.00	<b>NA</b>
16-6419	Stratum B; 173 ft downgradient from cliff, 10 ft south of drainage center.	RE16-00-1350	1	U	U	1	Sampled in September 2000, Middle RDX value in Stratum B cycle 1, set 2
16-6420	Stratum B; 215 ft downgradient from cliff, center of drainage.	RE16-00-1351	306	2	$\mathbf{1}$	309	Middle RDX value in Stratum B cycle 2, set 2
16-6421	Stratum B; 215 ft downgradient from cliff, 10 ft north of drainage center.	RE16-00-1352	301	21	U	322	<b>NA</b>
16-6422	Stratum B: 215 ft downgradient from cliff, 10 ft south of drainage center.	RE16-00-1353	$\mathbf{1}$	U	U	1	<b>NA</b>

**Table 2.2-1 (continued)** 

 $\alpha$  U = The chemical is classified as undetected.

 $b$  NA = Not analyzed.

#### **2.2.2 Field Investigation for Bromide Inventory Sampling**

On April 14, 1997, a bromide tracer was added to the TA-16-260 settling pond in order to better understand the movement of water and contaminants through the source area and to determine if the TA-16-260 settling pond was contributing contaminants to the TA-16 springs. The tracer was prepared by mixing 100 kg of potassium bromide (Sigma Aldrich) with 450 gal. of tap water. The solution was mixed using a submersible pump and then pumped into the settling pond. There was no standing water in the settling pond when pumping commenced. Care was taken to adjust the flow so that the tracer did not run down the drainage below the settling pond. After the solution was pumped, the tank was flushed with 400 gal. of tap water (200 gal. each on the next two consecutive days) to remove any residual bromide and to

"chase" the tracer into the vadose zone so that it was less prone to move via surface water. The initial bromide tracer concentration was 65,789 mg/L. Because the outfall was inactive, the only water available for tracer movement was local precipitation and stored water in the vadose zone.

Bromide monitoring of the springs was initially conducted daily, and then every other day, to determine bromide breakthrough. A few surface water samples were also collected in the 260 settling pond lower drainage on the relatively rare occasions when there was flow following a storm. Results of the spring sampling were reported in LANL (1998, 59891), and the results are briefly summarized here. Bromide was first detected in SWSC Spring during June 1997 and in Burning Ground Spring during August 1997. These results indicate relatively rapid movement of the tracer in unsaturated or variably saturated conditions. There is a strong indication of fracture flow because of the rapid transport and because of the spiked nature of the breakthrough curves in both springs (LANL 1998, 59891). Less than 2% of the total mass of bromide added (100 kg) was observed in the springs, and concentrations were always below 1 mg/L. Sampling at the drainage below the settling pond showed some bromide during early surface flow events, but it was minimal in terms of mass. To determine where most of the bromide mass resides and to understand current controls on the movement of contaminants, soil and tuff samples were collected and leached for bromide as part of the 260 outfall IM source area removal activity (LANL 2002, 73706).

Prior to the removal of the settling pond sediment, a trench was excavated to the depth of the sediment/tuff interface along the center axis of the settling pond. Thirty-two samples were collected from the trench and were field-analyzed for bromide and moisture content. The locations were based on random profiles and set intervals within the trench. Based on the screening bromide concentration and application of the RSS strategy (Patil et al. 1994, 59113), 8 of 32 samples were selected for off-site analytical laboratory analyses.

Borehole 16-06370 was drilled in the center of the former settling pond area after the removal of the sediment (Figure 2.2-1). Sixteen samples were collected from 5-ft-depth intervals and were field-analyzed for bromide, RDX, and percent moisture. Again, the RSS strategy was used to select 4 of 16 samples for off-site laboratory analyses. In addition, four additional biased samples were collected and submitted for off-site analysis of HE, bromide, and percent moisture.

Following a method similar to the American Society for Testing and Materials (ASTM) test method for soil pH (ASTM method D4972), a semiquantitative estimate of bromide concentration was made. A saturated paste was made from sample material and distilled water using a mortar and pestle. This saturated paste was measured with an Orion model 290A ion-specific electrode. The millivolt (mV) readings were recorded and compared to the mV readings for the 1.0 mg/kg and 10.0 mg/kg bromide calibration solutions. Bromide profiles for the eight trench profiles are shown in Figure 2.2-2. Profile 8 is from the western-most transect (upstream) and Profile 5 is from the eastern-most transect (downstream). Concentrations are generally lowest near the western part of the settling pond and increase downslope, with the center and eastern transects having bromide concentrations up to 41 mg/L. Because water was used during drilling, pore water concentrations were not calculated for Borehole 16-06370. However, the mass of bromide/mass of dry rock were calculated, and these values are plotted on Figure 2.2-3. There were only two samples with detectable bromide concentrations (0.1 and 0.8 µg/g). These samples were in the upper 20 ft of the borehole. No detectible bromide was reported below 20 ft.



**Figure 2.2-2. Pore water bromide in the SWMU 16-021(c)-99 settling pond. Profile 8 is on the upstream end of the settling pond; Profile 5 is on the downstream end.** 



**Figure 2.2-3. Bromide concentrations in Borehole 16-06370 pore water** 

As stated above, only a small fraction of the bromide tracer ended up in the two springs. This observation indicates that most of the bromide mass is stored in the vadose zone. An estimate of the vadose zone storage was obtained by examining how much bromide was present in the settling pond before the IM removal and how much was present after IM removal. Using a value of 357.8  $m^3$  for the amount of settling pond material removed (LANL 2002, 73706), a bromide concentration of 1.44 g/kg (the average concentration from the 8 trench profiles), and assuming a bulk density of 1.5 g/cm<sup>3</sup>, the estimated bromide mass in the settling pond is 257 kg. The estimate is ~2.5 times greater than the amount of tracer actually added. The overestimate is probably related to the higher bromide concentrations near the center of the settling pond, where the samples were collected, rather than on the sides of the settling pond (so the 1.44 g/kg value is probably too high). Nevertheless, the mass calculations and the bromide profiles themselves indicate the vast majority (approximately 98%) of bromide tracer was still in the top 4 ft of the settling pond sediment and tuff prior to the IM removal. Data from the springs and Borehole 16-06370 show some bromide moved into the deeper vadose zone/groundwater system, but this is a small fraction (approximately 2%) of the total mass.

In addition to verifying the connection between the 260 settling pond and the two springs, the bromide tracer study provides a good proxy for the behavior of contaminants such as RDX since the outfall became inactive in 1996. The bromide results indicate minor movement into the vadose zone, with some rapid transport to depth. Contaminants are probably moving in a similar fashion in that there is probably only slow movement for most of the contaminants in the vadose zone, with faster movement along preferential flow paths such as fractures or surge beds when they are encountered during migration. This behavior stands in strong contrast to what was the likely behavior when the outfall was active. At that time there was probably substantial movement of contaminants into and through the vadose zone because of the large amount of water being released which provided a hydrologic driving force for contaminant migration.

# **2.2.3 IM SAP Deviations and Augmentation**

The field implementation process described in the IM plan for the source area (LANL 2000, 64355.4) did not prescribe the June 2001 remobilization efforts undertaken to remove isolated areas where concentrations of HE greater than action criterion remained following the initial removal. These isolated areas of contamination were discovered following the September post-removal confirmation sampling. To ensure that concentrations of HE were below the action criterion following the second removal, a total of five screening samples were collected (one from each of the five isolated areas with HE above the action criterion). These samples were field-analyzed using an immunoassay method to verify that removals were successful; they were then further analyzed at an off-site contract analytical laboratory. The analytical laboratory analyses of these additional five samples included PCB analysis as well as the suite of analyses conducted for the original samples.

# **2.3 Results**

All post-removal source area characterization data are presented in the IM report (LANL 2002, 73706). The IM report includes a discussion of the overall analytical data quality and presents an analyte-byanalyte comparison with BVs (for inorganic chemicals) and detection limits (for organic chemicals). The IM report also presents tables summarizing the analytical results for all inorganic chemicals with concentrations exceeding BVs and for the detected organic chemicals. Because the IM report did not include a human health risk screening assessment, the data were not formally reviewed to identify inorganic and organic COPCs, and the report did not present the tables of chemicals retained/eliminated used to identify COPCs. The IM source area characterization data are interpreted and reviewed further in this report. The COPC retained/eliminated tables are presented below. These data serve as input data to the human health risk assessment, which is summarized in section 6.0 and detailed in Appendix K to this report.

## **2.3.1 IM Post-Removal and Bromide Inventory Data Review**

The review of the post-removal source area's inorganic chemical and organic chemical data are summarized in Table 2.3-1 and 2.3-2; the results of the bromide inventory are summarized in Table 2.3-3. The first two tables identify those chemicals in the 260 outfall source area that are either carried forward as COPCs or eliminated. For the post-removal sampling locations in isolated areas, it is important to note that only the samples collected following the secondary excavation of these areas were considered for the COPC identification process. The samples collected at these locations prior to the secondary excavation were excluded from consideration (although they are included in summary tables in the IM report) because they are no longer present and are not representative of current site conditions. Table 2.3-3 shows the analytical laboratory results for bromide concentrations in the eight samples collected from the source area prior to the IM removal and in the eight samples collected from Borehole 16-06370 underlying the source area.

## **2.3.2 Data Summary and Interpretation**

The 260 IM report presents a detailed interpretation of the post-removal source area data and includes trend plots for the major source area contaminants (LANL 2002, 73706). This discussion is summarized below.

The 260 IM significantly reduced the quantities of HMX, RDX, TNT, and barium throughout the source area and drainage channel. On a mass basis, the IM removed a total of 8500 kg of HE (total of HMX, RDX, and TNT). No barium mass could be calculated because no total metals analyses were performed on the waste-characterization samples. HMX, RDX, TNT, and barium remain the primary contaminants present in the 260 outfall drainage channel. Post-removal contamination may be summarized as follows (location IDs are shown in Figure 2.2-1):

- HMX remains in concentrations ranging from 2.2 to 2000 mg/kg (location 16-06409),
- RDX remains in concentrations ranging from 1 to1200 mg/kg (location 16-06379),
- TNT remains in concentrations ranging from 0.25 to 330 mg/kg (location 16-06379), and
- barium remains in concentrations ranging from 148 to 8200 mg/kg (location 16-06420) and is detected above the BV in all but one post-removal analytical sample.

Several additional HE compounds, HE-related compounds, and a few other organic compounds are present in the drainage channel, all at low concentrations (location IDs are shown in Figure 2.2-1): Amino-2,6-dinitrotoluene[4-] remains in concentrations in excess of 1 mg/kg (locations 16-06398, 16-06403, and 16-06402).





 $\Gamma$ 



# **Table 2.3-1 (continued)**

<sup>a</sup> ALLH = Soil All Data (may include soil and sediment).

 $b$  QBT3 = Unit 3 of the Quaternary Tshirege Member of the Bandelier Tuff.

c See Appendix I for further discussion.





 $a$  ALLH = Soil All Data (may include soil and sediment).

b QBT3 = Unit 3 of Quaternary Tshirege Member of the Bandelier Tuff.

Location <b>Identification</b>	<b>Sample</b> Identification	Collection Date	<b>Begin</b> Depth (ft)	<b>End Depth</b> (f <sub>t</sub> )	<b>Medium</b>	<b>Sample</b> <b>Results</b> (mg/kg)				
SOURCE AREA (PRE-IM)										
16-06362	RE12-00-0016	7/18/2000	$\Omega$	1.9	$\mathsf{SED}^a$	2.39				
16-06363	RE12-00-0017	7/18/2000	0.5	0.85	<b>SED</b>	1.04				
16-06364	RE12-00-0018	7/18/2000	1.4	1.7	<b>SED</b>	$0.12 U^{b}$				
16-06365	RE12-00-0019	7/18/2000	1.4	1.7	<b>SED</b>	0.957				
16-06366	RE12-00-0020	7/18/2000	1.7	2	<b>SED</b>	0.12U				
16-06367	RE12-00-0021	7/18/2000	0.7	1	<b>SED</b>	0.12U				
16-06368	RE12-00-0022	7/18/2000	2.7	3	<b>SED</b>	0.12U				
16-06369	RE12-00-0023	7/18/2000	0.5	0.75	<b>SED</b>	0.12U				
SOURCE AREA SUBSURFACE (POST-IM BOREHOLE)										
BH16-06370	RE12-00-0024	9/20/2000	9	10	QBT3 <sup>c</sup>	$0.024$ $UJd$				
BH16-06370	RE12-00-0025	9/23/2000	32	33	QBT3	$0.024$ UJ				
BH16-06370	RE12-00-0026	9/22/2000	19	20	QBT3	$0.932$ J- $^{\rm e}$				
BH16-06370	RE12-00-0027	9/20/2000	4	5	QBT3	$0.024$ UJ				
BH16-06370	RE12-00-0028	9/23/2000	36.5	37	QBT3	$0.024$ UJ				
BH16-06370	RE12-00-0029	9/28/2000	69	70	QBT3	$0.024$ UJ				
BH16-06370	RE12-00-0030	9/23/2000	41	41.8	QBT3	$0.024$ UJ				
BH16-06370	RE12-00-0031	10/2/2000	16.6	18.4	QBT3	$0.024$ UJ				

**Table 2.3-3 Results of Bromide Concentrations within the Source Area (Pre-IM) and Underlying the Source Area (Post-IM)** 

a SED = sediment.

 $b$  U = the chemical is classified as undetected.

c QBT3 = Unit 3 of Quaternary Tshirege member of the Bandelier Tuff Unit.

 $d$  UJ = the chemical is classified as undetected, with an expectation that the reported result is more uncertain than usual.

<sup>e</sup> J- = the chemical is classified as detected, but the reported concentration value is expected to be more uncertain than usual, with a potential negative bias.

Inorganic chemicals, besides barium, are also present in many samples that exceed two to seven times the BVs in soils. These metals are shown in Table 2.3-1 as COPCs.

Prior to the IM, spatial trends were observed in concentrations of the major contaminants in the drainage channel. These trends are discussed in detail in the Phase II RFI report (LANL 1998, 59891). In general, those contaminants present in the highest concentrations showed a marked decrease between the settling pond and the lower end of the drainage channel. The area of contamination also widened out in the midreaches of the drainage channel (between 200 and 600 ft downstream from the outfall) (LANL 1996, 55077). Contamination penetrated the tuff surface but contaminant concentrations were considerably higher in the overlying channel sediment (with the exception of the surge bed identified at a depth of 17 ft directly beneath the settling pond). Data from the Phase I RFI and Phase II RFI also indicate contaminant impacts were restricted to the well-defined drainage channel and did not intrude laterally into the channel overbank deposits to a great degree (LANL 1996, 55077; LANL 1998, 59891).

Following the IM, these previously identified spatial trends are no longer evident. Post-removal contamination tends to be spotty and variable. This variability indicates post-removal distributions are more affected by the success of the excavation than by the natural depositional processes that created the pre-IM spatial trends. The HE remains elevated in a small number of isolated locations randomly distributed throughout the drainage channel. Some of the highest concentrations of contaminants are now found in Stratum B between the base of the cliff and the drainage channel's confluence with Cañon de Valle. HE concentrations at the new (post-removal) drainage channel surface are now similar to concentrations observed in the underlying tuff. However, at location 16-06379, at the head of the settling pond in the center of the channel, the concentrations of HMX, RDX, TNT, and barium are higher in the underlying tuff than in the surface soils. Contaminants tend to have higher concentrations along the center axis of the channel than along the banks. In general, elevated concentrations of RDX, HMX, TNT, and barium occur at the same locations.

Post-removal data for the other organic and inorganic COPCs also indicate that the residual contamination remaining in the drainage channel occurs in isolated areas. Multiple contaminants are observed at a few locations. At location 16-6402 (the center of the channel, 360 ft downstream from the outfall), six organic chemicals and four inorganic chemicals were detected above BVs (the HMX concentration was also elevated). At location 16-6405 (the lower drainage in the center of the channel, 5 feet below the cliff), six organic chemicals were detected (the HMX concentration was also elevated). At location 16-6416 (the south side of the lower drainage, 131 ft below the cliff), six inorganic chemicals were detected above BVs. Seven organic compounds were detected (all qualified as J) at location 16-6403 (90 ft from the outfall, approximately 12 ft north of the channel axis). No other location had more than five inorganic chemicals detected above background or more than five organic chemicals detected, and no other location contains more than eight total COPCs.

To summarize, post-removal data indicate there are discrete areas of elevated contamination that do not show spatial trends. HMX, TNT, and barium are present in relatively high concentrations within these discrete areas, and RDX also remains elevated. The residual contamination remaining within the 260 outfall source is evaluated in the site-specific risk assessments (SSRAs) summarized in section 6 and detailed in Appendix K.

# **2.4 Implications for the TA-16 Hydrogeologic Conceptual Model**

The most significant implication for the TA-16 conceptual model is that the principal source of contamination (the TA-16-260 outfall drainage channel) affecting downgradient components of the site hydrogeologic system has been substantially reduced through the implementation of the IM. Approximately 8500 kg of HE were removed from the contaminant source area. Based on post-removal and historical data, it is estimated that approximately 650 kg of HE still remain in SWMU 16-021(c)-99 (LANL 2002, 73706). As the contaminant mass in this source area is decreased, it is anticipated contaminant mass in other components of the hydrogeologic system downstream will decrease. Remaining ongoing sources of contamination are either associated with historic HE releases elsewhere in TA-16 or are the downgradient system components, such as sediment, now acting as secondary sources of contamination.

The bromide data supports the idea that conservative contaminants, such as RDX, are slowly being transported from vadose zone reservoirs to downgradient water bodies. Fracture and surge bed transport are also suggested by the bromide tracer data. In the absence of a hydrologic driving force, as has been the case since the outfall was turned off, movement of conservative constituents such as RDX and bromide is likely to be slow. The potential impacts on alluvial groundwater and surface water quality are evaluated in the SSRA summarized in section 6.0 and detailed in Appendix K.

## **3.0 ALLUVIAL SYSTEM INVESTIGATION**

#### **3.1 Summary**

This section provides a summary of the alluvial investigation for Cañon de Valle and Martin Spring Canyon. Phase III alluvial investigation activities included

- characterizing subsurface and alluvial groundwater through installation of seven piezometers in Cañon de Valle and three alluvial groundwater wells in Martin Spring Canyon;
- determining contaminant dynamics and distribution through sampling of alluvial groundwater and surface water in Cañon de Valle and Martin Spring Canyon;
- determining contaminant inventory and distribution using geomorphic-based sediment sampling in both Cañon de Valle and Martin Spring Canyon;
- characterizing hydraulic interconnectivity and the residence time of water in the subsurface through a stable isotopes study; and
- investigating potential pathways for contaminant migration within the subsurface using geophysics studies.

The Cañon de Valle alluvial system dynamics are summarized as below.

#### Surface Water

The significant COPCs for Cañon de Valle surface water are RDX and barium.

- Oxygen isotope results show the alluvial groundwater and the surface water do not always follow the same trends, indicating that there are source differences between surface water and alluvial groundwater (although there is exchange between the two).
- There are losing and gaining reaches in Cañon de Valle. The water lost may move into storage in the alluvium or represent a source for recharge to the more deeply perched groundwater.
- RDX concentrations in the surface water in Cañon de Valle are highest near the 260 outfall area. The highest mass flow rate of RDX in surface water occurred during wet periods.
- Both barium and RDX were detected in surface water samples at the confluence with Water Canyon (approximately 3 mi downstream from the source area). This indicates the entire Cañon de Valle alluvial system contains RDX and barium.

#### Alluvial Groundwater

The significant COPCs for Cañon de Valle alluvial groundwater are RDX, barium, and manganese.

- The alluvial groundwater in Cañon de Valle appears to be connected throughout the saturated alluvium; however, differing head responses in the monitoring wells indicate heterogeneity within the alluvium.
- Barium concentrations are consistently higher in the alluvial groundwater than in the surface water.
- High resolution resistivity (HRR) geophysical surveys show a highly conductive region below the Burning Ground Spring wetland area. The surveys also show an approximately 20-ft-thick low resistance layer, dipping to the west, approximately 200 ft upstream from MDA P. This could be one potential zone of deeper infiltration from the alluvial system. Controlled source audio-

frequency magnetotelluric (CSAMT)/natural source audio-frequency magnetotelluric (NSAMT) geophysical surveys conducted to a depth of 1500 ft bgs indicate the presence of discrete, heterogeneous sub-vertical electrically conductive layers. The deep conductive zone appears to be bounded on the east, may be discontinuous in nature, and may represent preferential pathways such as surge beds or fracture zones.

- RDX concentrations for Well 16-02659 (located the farthest distance east from the 260 outfall) were consistently higher than concentrations for Wells 16-02655, 16-02656, and 16-02658 (see section 3.4.3).
- Barium concentration trends in alluvial groundwater over time are stable to slightly decreasing. Spikes associated with pulses of barium into the system may be due to sediment flushing.
- There is a positive correlation between saturated thickness in Cañon de Valle alluvial wells and RDX concentration, indicating RDX residing within the vadose zone constitutes an important secondary source and is released to the alluvial groundwater during periods of increased saturated thickness in the alluvium.

#### Sediment

The significant COPCs for Cañon de Valle sediment are RDX, HMX, amino-2,6-dinitrotoluene [4-], amino-4,6-dinitrotoluene [2-], TNT, antimony, barium, cobalt, copper, lead, nickel, and silver.

- The geomorphic investigation results support the existence of at least three Laboratory sources of barium for the sediment in Cañon de Valle: 1) a minor source upstream from MDA R, possibly SWMU 16-026(m), the outfall for the 90s Line building; 2) a larger source at, or in the vicinity of, MDA R; and 3) the 260 outfall.
- The resampling of a subset of the 1996 active channel locations in 2002 allowed a time comparison of barium and RDX concentrations. For barium, the reach immediately upstream of the 260 outfall and the reach downstream from the 260 outfall both had concentrations that were noticeably lower. For RDX, all reaches had lower concentrations in 2002, except the reach downstream from Well 16-02658.
- Immediately downstream from Location ID 16-05967 (Silver Seep), x-ray fluorescence (XRF) screening data reported silver concentrations of 2,595 and 957 mg/kg. Within the main reach of Cañon de Valle, 40 out of 46 samples exceeded the 1.0 mg/kg sediment BV for silver (LANL 1998, 59730).

Martin Spring Canyon alluvial system dynamics are summarized below:

The significant COPCs for Martin Spring Canyon surface water are RDX, barium, boron, and manganese. The COPCs for alluvial groundwater include RDX, arsenic, barium, beryllium, boron, cadmium, lead, and manganese.

The significant COPCs in Martin Spring Canyon alluvium, sediment, and tuff include amino-2,6 dinitrotoluene [4-], amino-4-6-dinitrotoluene [2-], RDX, TNT, arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, and silver.

• RDX was detected in the surface water and alluvial groundwater at locations in Martin Spring Canyon. Groundwater discharge from Martin Spring and the K-Site drop tower could be the primary sources for RDX in the canyon.

- Barium and RDX are both present in Martin Spring Canyon sediment, but at much lower concentrations and with much smaller inventories than in Cañon de Valle.
- The source for barium in Martin Spring Canyon sediment is located up the tributary drainage east of the TA-16 HE casting building 306. Concentrations decline downstream as mixing with other sediment sources occurs.

#### **3.2 Data Needs and Objectives**

The Phase I RFI data documented widespread HE contamination at SWMU 16-021(c)-99, extending from the 260 outfall discharge point down to the sediment and water of Cañon de Valle. The Phase II RFI data documented widespread HE contamination extending from the 260 outfall discharge point down to the sediment and water of Cañon de Valle and showed deeper subsurface contamination. The purpose of the Phase III RFI alluvial system investigation is to provide critical site data input to the CMS by further characterizing the nature and extent of contamination. CMS data requirements for the alluvial systems were presented in the CMS plan (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2) and included the broad investigative questions described below.

*What is the hydraulic connectivity between the 260 outfall and the TA-16 springs and seeps; are there other transport pathways connected directly to perched groundwater and regional groundwater?* 

• In 1999 and 2001 geophysical surveys were conducted by hydroGEOPHYSICS, Inc. to characterize the saturated alluvium and potentially identify losing reaches in Cañon de Valle using HRR and refraction seismic (RS) surveys. In September 2002, Zonge Engineering and Research Organization (Zonge) completed CSAMT and NSAMT survey work to identify potential saturated zones and transport pathways at depths up to 1500 ft bgs.

*How long does it take water to travel from the discharge point (260 outfall) to the TA-16 springs and seeps (residence time)?* 

- Stable isotope analyses were performed on precipitation samples, alluvial water samples, and on spring/seep samples (see section 4.0) to characterize the residence times and the connectivity of the alluvial system.
- Potassium bromide tracer inventory was conducted at the source area (see section 2.2.2).

*What are the alluvial system dynamics?* 

- Surface and subsurface discharge profiles were measured for the perennial reach of Cañon de Valle and the upper reach of Martin Spring Canyon to input into the water balance characterization of each of the alluvial systems.
- Surface water was sampled approximately five times per year in Cañon de Valle and Martin Spring Canyon; samples were analyzed at an off-site laboratory for HE, metals, VOCs, SVOCs, stable isotopes, and water quality parameters.
- Three alluvial wells were installed in Martin Spring Canyon to characterize the alluvial system dynamics; one below the spring, one in the saturated area below K-Site, and one down-drainage from the saturated area.
- Seven shallow piezometers were installed in Cañon de Valle alluvium to identify the perennial reach in the canyon bottom.

• Alluvial wells in Cañon de Valle and Martin Spring Canyon were sampled quarterly; samples were analyzed at an off-site laboratory for HE, metals, VOCs, SVOCs, stable isotopes, and water quality parameters.

#### *What are the alluvial sediment dynamics?*

- Geomorphic mapping and sampling of the overbank and channel deposits were conducted in reaches of Cañon de Valle and Martin Spring Canyon to characterize the inventories of contaminants in the deposits and evaluate the mobility of these deposits. Soil/sediment/tuff samples were analyzed at an off-site laboratory for HE and HE-breakdown products (EPA Method 8330); for metals including boron (EPA Method 6010B/6020); and for SVOCs (EPA Method 8270c).
- Field screening was conducted on soil/sediment/tuff and water samples. Soil/sediment/tuff samples were field-screened for bromide, percent moisture, and HE. Water samples were fieldscreened for temperature, pH, and specific conductance.

## **3.3 Scope of Phase III Sampling and Analysis**

The alluvial system for SWMU 16-021(c)-99 includes two canyons: Cañon de Valle and Martin Spring Canyon. Both are tributaries of Water Canyon (Figure 3.3-1). The alluvial system within each canyon can be divided into two components: water and sediment. The alluvial water was sampled from two zones: surface water and alluvial groundwater. The alluvial sediment (including soil, sediment, and tuff) was sampled from the active channel; the floodplain; and shallow boreholes. Aquatic and terrestrial samples were collected to support a baseline ecological risk assessment in Cañon de Valle only. Figure 3.3-1 shows all locations sampled during the period from 1998 through 2002 that are associated with the Phase III alluvial systems RFI.

Water samples were collected from bucket gauges following precipitation events, as grab samples from surface water, natural springs (see section 4.0) and seeps, and alluvial groundwater wells at various locations around TA-16. Sediment samples were collected from both from surface and subsurface horizons. Surface soil and sediment are sampled during the geomorphic investigation. Subsurface horizons were primarily sampled during drilling operations. Sample collection and handling were performed as detailed in the SAP for the Phase III RFI, contained in the CMS plan (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2) and in conformance with the following standard operating procedures (SOPs), quality procedures (QPs), and other documents.

- Site-Specific Health and Safety Plan 01-001
- LANL ER-SOP-1.01, General Instructions for Field Investigations,
- LANL ER-SOP-1.02, Sample Containers and Preservation,
- LANL ER-SOP-1.03, Handling, Packaging, and Shipping Samples,
- LANL ER-SOP-1.04, Sample Control and Field Documentation,
- LANL ER-SOP-1.05, Field Quality Control Samples,
- LANL ER-SOP-1.07, Operational Guidelines for Taking Soil and Water Samples in Explosive Areas,
- LANL ER-SOP-6.01, Purging and Sampling Methods for Single Completion Wells,
- LANL ER-SOP-6.02, Field Analytical Measurements of Groundwater,
- LANL ER-SOP-6.03, Sampling for Volatile Organic Compounds in Groundwater,
- LANL ER-SOP-6.09, Spade & Scoop Method for Collection of Soil Samples,
- LANL ER-SOP-6.13, Surface Water Sampling,
- LANL ER-SOP 10.06, High Explosives Spot Test,
- LANL ER-QP-5.2, Control of Measuring and Test Equipment,
- LANL ER-QP-5.7, Notebook Documentation for Environmental Restoration Technical Activities,
- LANL ER-QP-10.3, Stop Work and Restart, and
- LANL-ER-QMP, Quality Management Plan for the Environmental Restoration Project.

#### **3.3.1 Surface Water Sampling and Analysis**

Surface water discharge, pH, temperature, conductivity, and chemical concentrations were measured during different surface water flow regimes to assist in characterizing the water and contaminant mass balance study described in the CMS plan (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2) and outlined in Table 1.4-1 as information needed to characterize the alluvial water dynamics.

#### **3.3.1.1 Surface Water Discharge Measurements**

Surface water discharge measurements were collected approximately 5 times per year in Cañon de Valle and Martin Spring Canyon. Surface water sampling was conducted on an event-basis in conjunction with measuring stream profiles (SPs). The first SP was measured in June of 1998. Other surface water samples were collected in 1994, 1996, and 1997 during the Phase II RFI (LANL 1998, 59891). Discharge measurements were collected representing the following flow conditions: runoff from snowmelt (typically in late March and April), dry season with low flow in perennial reaches (May to June), early monsoon (July), late monsoon (August to September) and fall post-monsoon (October to November). Surface water flow events in ephemeral reaches of the canyons resulted from snowmelt, prolonged frontal rainstorms, or consecutive convective rainstorms. A summary of regional and site-specific precipitation data is provided in Appendix B to this report.

In Cañon de Valle, there are 15 gauging stations (identified as SP#2 through SP#16) established along a 6000-ft-long stretch of canyon. In Martin Spring Canyon there are 6 stations (SP#1 through SP#6) along a 4000-ft-long stretch of canyon. These SP locations are identified on Figure 3.3-2.

Surface water discharge was calculated using stage measurements from a portable Parshall flume (Bureau of Reclamation 1997, 76890) or measured directly by collecting water in a calibrated-volume container and measuring the container fill rate with a stop-watch. At each gauging station, field parameters were measured approximately quarterly, or in response to specific flow events. The following field parameters were measured: discharge in L/sec, pH in standard units, conductivity as microsiemens (ms)/cm, and temperature in degrees Celsius (°C). Temperature, pH, and conductivity were measured using a Horiba multisensor probe.





**Figure 3.3-2. Sampling locations and identification numbers for surface water, springs, and groundwater samples** 

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### **3.3.1.2 Field Screening, Surface Water Sampling, and Off-Site Laboratory Analysis**

Field screening for barium, RDX, and bromide was conducted on all surface water samples submitted for laboratory analysis. Barium was analyzed using a HACH probe, RDX using Dtech immunoassay/ colorimetric methods, and bromide using a standard solution and HACH instrument.

Following each field-screening event, the sampling team reviewed the field-screening results and determined which locations would be sampled and shipped for off-site laboratory analysis. Generally, the farthest up-canyon and down-canyon locations were sampled in addition to any conspicuous gaining or losing locations determined from discharge measurements. Typically, between three to six surface water samples were collected In Cañon de Valle. In Martin Spring Canyon, three surface water samples were collected. The samples were analyzed for alkalinity (EPA Method 310.1/310.2), anions and perchlorate (EPA Method 314), nitrate/nitrite (EPA Method 300.1/9056), HE (and HE-breakdown products) (EPA Method 8330), and metals (EPA Method 6010B/6020). All surface water samples were unfiltered, with the exception of samples analyzed for metals that included both filtered and unfiltered sample aliquots. Table 3.3-1 summarizes the annual sampling and analysis for surface water in Cañon de Valle and Martin Spring Canyon. Table 3.3-2 lists the location IDs for the surface water samples. Figure 3.3-3 shows field personnel collecting surface water samples. A summary of all laboratory analyses requested for surface water samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3.

### **Table 3.3-1 Summary of Annual Sampling and Analysis of Surface Water in Cañon de Valle and Martin Spring Canyon**



*Note:* Modified from Table 6.3-4 of the SAP (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2).

\*n/a = Not applicable.

**Table 3.3-2 List of Surface Water Sample Locations for Cañon de Valle and Martin Spring Canyon** 

Location ID*	Sample Location*				
Cañon de Valle					
16-05968	Headwaters of Cañon de Valle				
16-06121	Confluence of Cañon de Valle and Fishladder Canyon				
16-05969	Confluence of Cañon de Valle and Water Canyon				
16-05970	Water Canyon at ESH-18 weir				
16-05993	Stream Profile Location 2 Cañon de Valle				
16-05994	Stream Profile Location 3 Cañon de Valle				
16-05995	Stream Profile Location 4 Cañon de Valle				
16-05923	Stream Profile Location 5 Cañon de Valle				
16-05926	Stream Profile Location 6 Cañon de Valle				
16-05927	Stream Profile Location 7 Cañon de Valle				
16-06500	Near 16-05927, RE16-00-3214				
16-05996	Stream Profile Location 8 Cañon de Valle				
16-05997	Stream Profile Location 9 Cañon de Valle				
16-05998	Stream Profile Location 10 Cañon de Valle				
16-02768	Cañon de Valle main channel near Stream Profile Location 10				
16-02770	Cañon de Valle main channel between Stream Profiles Locations 10 and 11				
16-05999	Stream Profile Location 11 Cañon de Valle				
16-05928	Stream Profile Location 12 Cañon de Valle				
16-05929	Stream Profile Location 13 Cañon de Valle				
16-05600	Stream Profile Location 14 Cañon de Valle				
16-05930	Stream Profile Location 15 Cañon de Valle				
16-05601	Stream Profile Location 16 Cañon de Valle				
16-02654	Fishladder Seep				
16-02653	Peter Seep				
16-05967	Silver Seep				
16-06709	XRF#2, Cañon de Valle, Ecotoxicological sample #1 (Figure 3.3-10)				
16-06710	XRF#5, Cañon de Valle, Ecotoxicological sample #2 (Figure 3.3-10)				
16-06711	XRF#9, Cañon de Valle, Ecotoxicological sample #3 (Figure 3.3-10)				
<b>Martin Spring Canyon</b>					
16-05920	Stream Profile Location 1 Martin Spring Canyon				
16-05921	Stream Profile Location 2 Martin Spring Canyon				
16-05988	Stream Profile Location 3 Martin Spring Canyon				
16-05989	Stream Profile Location 4 Martin Spring Canyon				
16-05990	Stream Profile Location 5 Martin Spring Canyon				
16-05991	Stream Profile Location 6 Martin Spring Canyon				
<b>Starmer's Gulch</b>					
16-06712	Starmer's Gulch (Background ecotoxicological sampling; Figure 3.3-10)				

\*Location ID and sample location are presented on Figure 3.3-2 and Figure 3.3-10.



**Figure 3.3-3. Field Personnel collecting water samples at Location ID 16-05968, located in Cañon de Valle headwaters (location provided on Figure 3.3-2). Photo was taken in June 2002, view looking west (upstream).** 

### **3.3.1.3 Deviations**

The intent of the SP sampling was to collect samples representing different flow regimes under normal climatic conditions (LANL 1998, 62413.3). Historic climate records show periods of summer rain and spring snowmelt runoff (Bowen 1990, 06899). However monthly precipitation totals were well below average during the period from 1998 to 2002 (Appendix B), due to draught conditions. As a result, fewer SP samples were collected than directed by the SAP because there were limited flow events.

### **3.3.2 Alluvial Groundwater Sampling and Laboratory Analysis**

#### **3.3.2.1 Monitoring Well Instrumentation and Groundwater Measurements**

#### Cañon de Valle Wells

Six shallow alluvial wells were drilled in the fall of 1997 in conjunction with the Phase II RFI. They are designated as follows: 16-02655, 16-02656, 16-02657, 16-02658, 16-02659, and 16-02660. Alluvial well locations are shown on Figure 3.3-2. In June 1999, each well (with the exception of 16-02657, as the well is frequently dry) was equipped with a battery-powered data logger to continuously record water level, conductivity, and temperature. The locations of the wells are listed below.

- Well 16-02655 is located in the Cañon de Valle upland area in the steam plant drainage.
- Well 16-02656 is located within the canyon bottom, near MDA R.
- Well 16-02657 is located within the canyon bottom just downstream of the 260 outfall confluence with Cañon de Valle.
- Well 16-02658 is located within the middle reach of the canyon bottom, and downstream of SWSC and Burning Ground Springs.
- Well 16-02659 is located at the lower reach of the canyon bottom downstream of MDA P.
- Well 16-02660 is located adjacent to Well 16-02659 at the lower reach of the canyon bottom downstream of MDA P. Well 16-02660 was designed and installed for physical testing of the groundwater and therefore no datalogger was installed. This location has not been used to collect water samples.

All wells were drilled to a total depth of approximately 10 ft bgs into the soil-tuff interface. The wells are 2 in.- or 4-in.-diameter polyvinyl chloride and screened in the bottom 5-ft interval. The screened interval included the soil-tuff interface for all wells. Detailed well completion diagrams and borehole logs can be found in Appendix G of the Phase II RFI Report (LANL 1998, 59891). Figure 3.3-4 shows field personnel at Well 16-02658.

### Martin Spring Canyon Wells

Three wells were drilled in Martin Spring Canyon in January 2000 and they are designated 16-06293, 16-06294, and 16-06295. Complete well completion diagrams and drilling logs are included in Appendix C. Well 16-06293 is located approximately 2000 ft downstream of Martin Spring; Well 16-06295 is located furthest downstream near the K-Site drop tower; and Well 16-06294 is located approximately midway between Wells 16-06293 and 16-06295. Well locations are shown on Figure 3.3-2. These wells are not equipped to record data automatically. Monthly measurements of temperature, conductivity, pH, and water elevation were made using a hand held Horiba multisensor probe and a manual well sounder. Figure 3.3-5 shows field personnel at Well 16-06295 in Martin Spring Canyon.

# **3.3.2.2 Groundwater Monitoring Well Sampling and Offsite Laboratory Analysis**

The alluvial wells were sampled as part of the quarterly sampling campaign that began in December of 1997 (LANL 1996, 55077). The five wells in Cañon de Valle and three wells in Martin Spring Canyon were sampled quarterly in approximately March, June, September, and December. In March, there were normally wet conditions following the spring snowmelt. The June sampling usually represented dry, low flow conditions. If there were normal summer monsoons, conditions in September were wet. December sampling was usually marked by low flow conditions.

The alluvial wells in Cañon de Valle and Martin Spring Canyon were sampled in accordance with LANL-ER-SOP 6.01 Purging and Sampling Methods for Single Completion Wells. As part of the sampling process, pH, conductivity, and temperature were monitored throughout the sampling process. Initial depth to water and the final stabilized temperature, conductivity, and pH were noted on the sample collection logs. Additionally, as directed by the CMS plan (LANL 1998, 62413.3) field-screening for barium, RDX, and bromide was conducted on all water samples submitted for laboratory analysis. Barium was analyzed using a HACH probe, RDX using Dtech immunoassay/colorimetric methods, and bromide using a standard solution and HACH instrument.



**Figure 3.3-4. Field personnel conducting monthly field measurements at Well 16-02658 in Cañon de Valle. Photo was taken in November 2002. View is looking down canyon. A piezometer nest (Locations 16-02459 and 16- 02460) is also visible to the left of the well housing.** 



**Figure 3.3-5. Field personnel conducting field measurements at Well 16-06295 in Martin Spring Canyon. Photo was taken in April of 2001, view looking downstream to the east.** 

The samples collected for off-site laboratory analysis were analyzed for: alkalinity (EPA Method 310.1/310.2), anions and perchlorate (EPA Method 314), nitrate/nitrite (EPA Method 300.1/9056), nitrogen isotopes (N<sup>15</sup>N<sup>14</sup>), low level tritium (LH<sup>3</sup>), hydrogen isotopes (D<sup>2</sup>H), oxygen isotopes (O<sup>18</sup>/O<sup>16</sup>), volatile organic compounds (EPA Method 8260B), total uranium (EPA Method 6020), HE (and HE breakdown products) (EPA Method 8330), metals including boron (EPA Method 6010B/6020), and once a year samples were collected for SVOC (EPA Method 8270C). All samples were unfiltered with the exception of metals that included both a filtered and unfiltered sample. Table 3.3-3 summarizes the annual sampling and analysis requirements for alluvial groundwater water in Cañon de Valle and Martin Spring Canyon. Location IDs for alluvial wells correspond to the well numbers and are shown on Figure 3.3-2. A summary of all laboratory analyses requested for alluvial groundwater samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3.



# **Table 3.3-3 Summary of Annual Sampling and Analysis for Alluvial Groundwater in Cañon de Valle and Martin Spring Canyon**

*Note:* Modified from Table 6.3-4 of the SAP (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2). \*n/a = Not applicable.

# **3.3.2.3 Deviations**

The alluvial wells in Cañon de Valle and Martin Spring Canyon were sampled in accordance with LANL-ER-SOP 6.01. One deviation from this method was during the dry seasons, when wells were not purged until screening parameters stabilized. A typical single round of sampling required approximately 10 L of water. Often only partial samples were collected because there was less than 10 L of water available in the well casing and the dry conditions precluded timely recharge of the well.

# **3.3.3 Alluvial System Characterization**

This subsection describes the methodology for geophysical surveys, piezometer installation, seep dynamics, precipitation data collection, and stable isotope analyses in the Cañon de Valle and Martin Spring Canyon alluvial systems.

# **3.3.3.1 Geophysical Surveys**

In 1999 and 2001, geophysical surveys were conducted by hydroGEOPHYSICS, Inc. to characterize the alluvial system in Cañon de Valle. In 1999, HRR and RS surveys were conducted at Cañon de Valle. The objective of these first surveys was to detail the extent and degree of saturation of alluvium in the canyon bottom. Two survey lines, designated 2658 Line and 2659 Line, were oriented perpendicular to the canyon drainage (Figure 3.3-6). These survey lines were located near Wells 16-02658 and 16-02659 to provide controlled information on alluvium saturation. The survey methodology is detailed in the 1999 geophysical survey report provided in Appendix D-1.

In 2001, the HRR and RS surveys were continued with additional emphasis on HRR. Two perpendicular transects from 1999 were repeated and a third perpendicular survey line was added near SP#16, 16-05601 (Figure 3.3-6). A longitudinal profile survey was conducted that extended from upstream of Burning Ground Spring to approximately 900 ft downstream from Well 16-02659. The longitudinal line roughly paralleled the stream channel and was designed to help identify potential vertical losing zones in the canyon. Figure 3.3-6 shows the locations of the HRR lines. The 2001 geophysical survey report is provided in Appendix D-2.

In September 2002, CSAMT and NSAMT survey work at TA-16 was completed. The survey was conducted to identify potential saturated zones at depths of up to 1500 ft bgs. Additionally, potential transport pathways associated with SWMU 16-021(c)-99 might also be identified. Both CSAMT and NSAMT data were collected. Eight combined survey lines were completed at TA-16, for a total coverage of 28,800 ft. The locations of the eight survey lines are shown on Figure 3.3-7. The complete report is provided in Appendix D-3.

# **3.3.3.2 Piezometer Installation**

Seven piezometers were installed in Cañon de Valle during September and October 2001 to characterize the extent of saturation in the alluvium. The piezometers consisted of 5-ft lengths of 1-in.-diameter steel pipe. The piezometers were installed directly into the alluvium using a post-hole driver and driven until refusal, between 1 to 4 ft bgs. To prevent sediment from clogging the end of the pipe, a solid steel rod was inserted into the pipe during installation. Following installation, the rod was removed from the center of the pipe.

Piezometer 16-02468, located 7300 ft downstream of the 260 outfall, was installed approximately 100 ft west of the Qbt 3/2 contact to a depth of 2 ft below grade in an alluvial flood plain deposit (Figure 3.3-2). Upstream, near SP#16, piezometer 16-02461 was installed to a depth of 2 ft below grade in an alluvial floodplain deposit. Piezometer 16-02466 was installed near Well 16-02659 to a depth of approximately 4 ft below grade on the south slope of the canyon. This mid-slope location was chosen based on geophysical data that indicated a possible saturated zone. At the final two locations, adjacent to Wells 16- 02658, and 16-02659, a piezometer nest was installed adjacent to each well. Near Well 16-02658 a piezometer nest was installed with one piezometer (16-02460) at 2 ft and the second piezometer (16- 02459) at 2.9 ft bgs. At Well 16-02659, one piezometer (16-02464) was installed at 2 ft









and the second piezometer (16-02466) was installed at 4 ft bgs. The intent of the installation of these nested piezometers was to measure vertical gradients. Piezometer locations are shown on Figure 3.3-2.

# **3.3.3.3 Peter Seep Dynamics**

The NMED-approved SAP (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2) requires the location of the 'foot' (the lower outlet) and 'head' (the upper outlet) of Peter Seep be documented. The location of the head of Peter Seep fluctuates within a reach of Cañon de Valle that is approximately 600 ft long. The head is approximately 500 ft upstream from the 260 outfall confluence and the foot (Location ID 16-02653) is approximately 50 ft downstream from the 260 outfall confluence. Figure 3.3-8 shows the foot of Peter Seep in 2000.

The behavior of Peter Seep was observed during the quarterly sampling events by measurements of location and discharge at the foot of Peter Seep, together with concurrent measurements of water levels in the alluvial wells installed during the Phase II RFI (LANL 1998, 59891) The resulting spatial patterns and correlations were analyzed to determine whether the location of Peter Seep varies along a continuum or is confined to discrete locations, and whether or not it is correlated with water elevation in the alluvial wells.

Concurrently with Peter Seep head and foot measurements, water levels were measured in the alluvial wells (see section 3.3.2.1) and discharge at the foot of the seep was recorded. Filtered grab water samples at the head and foot of the seep were also collected during the quarterly sampling events, and the standard field measurements (pH, temperature, and conductance) were performed on each of these samples. A summary of the sampling and analysis for Peter Seep is provided in Table 3.3-4. A summary of all laboratory analyses requested for Peter Seep water samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3.

# **3.3.3.4 Precipitation Stable Isotopes**

Precipitation samples were collected at the TA-16 field trailers for stable isotope analysis during precipitation events (Figure 3.3-2). Stable isotope analyses were performed to characterize the residence times and subsequently the connectivity of the alluvial system. The RRES-RS Water Quality and Hydrology (WQG) group provided precipitation records for TA-16 for the study period. The precipitation records are provided in Appendix B. The precipitation data complement the stable isotope study and put into context the hydrologic conditions during the study period.

Samples for stable isotope analysis were collected for possible analysis every-other day at Burning Ground Spring (560 samples), SWSC Spring (521 samples), and Martin Spring (554 samples) (see section 4.0) and at Peter Seep (60 samples) over a period of 3 years. The samples were collected in conjunction with the samples collected for the ongoing bromide tracer study (see section 2.2.2). Concurrently with the Phase III sampling period (nominally 2 to 3 years), precipitation samples were collected for stable isotope analysis at a station located near the TA-16 field trailers (Figure 3.3-2). Precipitation sampling is event driven. All precipitation samples were analyzed for the stable isotopes,  $δ<sup>18</sup>O$  and  $δD$  (Table 3.3-5). Nitrogen isotopes ( $δN$ ) were also analyzed for a subset of these samples, two per season. The precipitation data are used to establish isotope signatures of storms and the timing of atmospheric transitions.



**Figure 3.3-8. Photo of Location ID 16-02653, Peter Seep foot (location shown in Figure 3.3-2). Photo taken in June 2000, following the first major storm after the Cerro Grande fire. View is looking downstream.** 

<b>Sample or Survey Measurement</b>	<b>Number</b> <b>Collected</b>	<b>Number</b> Analyzed	<b>Field Measurements and Analytical Suites</b>
Record Peter Seep location	20	$n/a^*$	Discharge recorded
Record alluvial water elevations	20	n/a	Part of alluvial groundwater quarterly monitoring program
Filtered grab samples from head	$\overline{2}$	2	Field temperature, pH, conductance
of Peter Seep		2	HE, metals, nitrate/nitrite, anions, perchlorate, and alkalinity
Filtered grab samples from foot of	-20	20	Field temperature, pH, conductance
Peter Seep		3	HE, metals, nitrate/nitrite, anions, perchlorate, and, alkalinity

**Table 3.3-4 Summary of Annual Sampling and Analysis for the Investigation of Peter Seep Dynamics** 

*Note:* Modified from Table 6.3-4 of the SAP (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2). \*n/a = Not applicable.





*Note:* Modified from Table 6.3-2 of the SAP (LANL 1998, 62413.3; LANL 1999, 64873.3; LANL 2003, 75986.2).

#### **3.3.3.5 Deviations**

#### Geophysical Surveys

Longitudinal HRR profiles were not specifically called out in the CMS plan. However, based on the favorable results of the first longitudinal line, the coverage was extended past Well 16-02659.

#### Piezometer Installation

Two additional piezometers were installed for a total of seven piezometers. The CMS plan targeted the reach downstream of Well 16-02659. Because of the dry conditions during the monitoring period, these piezometers were typically dry. To target the wetter regions, two piezometers nests were installed (one nest each) adjacent to Wells 16-02658 and 16-02659.

#### Peter Seep Dynamics

After initial investigation of the Peter Seep head and foot location, it was determined the location of the foot was essentially stable. Water was at the head only following prolonged precipitation events or from snowmelt. During the monitoring period, these conditions were very rare. The head and foot of Peter Seep also corresponded respectively to the Location ID 16-05993 (SP#2) and Location ID 16-05995 (SP#4; Figure 3.3-2). These locations were monitored during changing hydrologic regimes when there would be the most likely chance for chemical or contaminant variations. Additionally, both the head and foot were included as sample locations during quarterly sampling. This combination provided the potential for 10 analytical samples per year. However, the dry conditions resulted in far fewer samples.

Following review of historical anion and stable isotope data indicating consistent data results, routine sampling at SWSC Spring and Peter Seep was discontinued in the Spring of 2001. A limited number of nonroutine anion and stable isotope samples were collected from these two locations subsequent to this date.

### **3.3.4 Sediment Sampling**

Phase II RFI sampling (LANL 1998, 59891) demonstrated that secondary sources of contaminants reside in both the active channels and in the overbank sediment of Cañon de Valle. However, very few samples had been collected outside the active channel, so neither the distribution nor the total inventory of contamination in the alluvial sediment could be estimated. Alluvial sediment had not been sampled in

Martin Spring Canyon. Channel sediment locations sampled during the Phase I RFI (LANL 1996, 55077) were resampled. A geomorphic study was conducted in both Cañon de Valle and Martin Spring Canyon to characterize the occurrence and distribution of contaminants in the alluvial deposits.

# **3.3.4.1 Cañon de Valle Active Channel Resampling**

To evaluate contaminant mobility in the sediment, a subset of the 1996 active channel sediment samples were resampled. A total of nine locations were chosen and one field duplicate sample was collected. Samples were collected from the following locations in July 2002: 16-02749, 16-02753, 16-02754, 16-02762, 16-02766, 16-02767, 16-02770, 16-02775, and 16-02777 (Figure 3.3-9). Locations were resampled and submitted for off-site laboratory analysis based on the concentrations of COPCs in Phase I RFI results (LANL 1996, 55077). Each sediment sample submitted to an off-site laboratory was analyzed for HE and HE-breakdown products (EPA Method 8330), metals including boron (EPA Method 6010B/6020) and SVOCs (EPA Method 8270c). A summary of all laboratory analyses requested for these sediment samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3.

# **3.3.4.2 Geomorphic Mapping and Sediment Sampling**

Sediment deposits less than 50 years old may contain contaminants released from SWMU 16-021(c)-99 or other TA-16 HE production facilities. Finer-grained sediment may have higher concentrations of contaminants than coarse-grained sediment. Contaminant levels could be particularly elevated in relatively fine-grained sediment deposited by unusually high flood events during the period of greatest discharge from the 260 outfall, if such sediment deposits can be identified. Therefore, geomorphic units in the canyon bottom of Cañon de Valle and Martin Spring Canyon were mapped to characterize the occurrence and distribution of contaminants as related to channel processes. Geomorphic mapping was performed in accordance with the methods provided in "Core Document for Canyons Investigations" (LANL 1997, 55622).

Subsequent sediment sampling was confined to areas found to include post-1942 sediment deposits, and stratified within such areas according to the results of the geomorphic survey. Geomorphic units were characterized by digging soil pits in each unit. Soil texture, color, and thickness were recorded for each soil layer. Each layer was also screened for barium and silver by XRF; and for RDX by Dtech kit. Following this, a statistician determined the number of samples for laboratory analysis to represent the contaminant inventory. Representative sediment samples were collected and analyzed for each geomorphic unit. Contaminant inventories were then calculated by multiplying the sediment concentration by the approximate volume of each geomorphic unit.

### Cañon de Valle

Geomorphic mapping and sampling of Cañon de Valle sediment was conducted in September 1999. The mapping of Cañon de Valle was conducted from the silver outfall (Figure 3.3-2) approximately 4000 ft downstream. The remainder of the canyon will be mapped as part of the canyons team investigation. Field-screening was completed on a total of 59 samples at 21 locations (Figure 3.3-9); 30 of these samples were selected using an RSS strategy and were analyzed for HE (EPA Method 8330), metals including boron (EPA Method 6010B/6020), and particle-size distribution (Janitzky 1986, 57674) at off-site laboratories. A summary of the laboratory analyses requested for the sediment samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3. Seven of these locations were resampled in July 2000 as part of a Laboratory CMS barium stabilization study (in progress). These seven



Sediment sampling locations **Figure 3.3-9. Sediment sampling locations** Figure 3.3-9. samples were also analyzed for metals by toxicity characteristic leaching procedure and for SVOCs in addition to the suite of analyses listed above.

#### Martin Spring Canyon

Geomorphic mapping and sampling of Martin Spring Canyon sediment was conducted in September 2000. The mapping extended downstream of Martin Spring for a distance of approximately 2000 ft. The remainder of the canyon will be mapped as part of the canyons team investigation. A total of 21 samples from 19 locations were sampled (Figure 3.3-9) and analyzed for HE (EPA Method 8330), metals including boron (EPA Method 6010B/6020), and particle-size analysis (Janitzky 1986, 57674). No screening data were obtained from Martin Spring Canyon. A summary of the laboratory analyses requested for the sediment samples is provided in Appendix G-1. A summary of all analytical data is provided in Appendix G-3.

### **3.3.5 Sampling to Support the Baseline Ecological Risk Assessment**

Several sampling campaigns were conducted to support the assessment of adverse effects to biota in Cañon de Valle from contaminants of potential ecological concern (COPECs). The list of COPECs, and the details of the sampling designs are provided in Appendix L. An overview of the sampling for the aquatic and terrestrial systems follows.

### **3.3.5.1 Aquatic System Sampling**

Two types of samples were collected to evaluate the aquatic system in the canyon. Co-located sediment and water samples were collected for toxicity testing with *Chironomus tentans.* This sampling was conducted in September 2001, July 2002, and December 2002. Benthic macro-invertebrates were collected to assess that community in the canyon relative to three reference streams in the area (Figure 3.3-10) in May 1997 and June 2001.

The toxicity testing samples consisted of 1-gal. sediment samples and 5-gal. water samples that were sent to the testing laboratory. All toxicity testing was performed in accordance with EPA Method 100.2 (EPA 2000, 73776), for a ten-day test with survival and growth measurement endpoints using eight replicates for each site. The first round of toxicity testing used site sediment and static renewal with site water. Samples were collected in three locations in Cañon de Valle and one location at a reference location in Starmer's Gulch. The Cañon de Valle locations (Figure 3.3-10) are 16-06709, SWSC Cut, a roadcut for the SWSC pipeline located downstream of SWSC Spring; 16-06710, below the confluence of Burning Ground Spring; and 16-06711, below MDA P. The Starmer's Gulch site is designated 16-06712. Splits of the sediment and water samples were submitted to the analytical laboratory for contaminant analysis. The suites were TAL metals (EPA Method 6010B/6020) and HE (EPA Method 8330). These data are used to interpret the toxicity test results.

The second and third rounds of toxicity testing were conducted to identify the source of toxicity associated with 16-06709, the SWSC Cut site from the first round of testing and to further evaluate test survival for Location ID 16-06710, below Burning Ground Spring. Sediment and water samples were collected as before. One set of toxicity test replicates for 16-06709 was conducted with site sediment and site water. A second set of replicates for that site was conducted with site sediment and testing laboratory reconstituted water. The Burning Ground Spring site, 16-06710, and Starmer's Gulch site, 16-06712, were tested with site sediment and site water.



**Figure 3.3-10. Location of ecotoxicology sampling in Cañon de Valle** 

Personnel of the NMED Oversight Bureau conducted the benthic macroinvertebrate sampling. The methods are consistent with the protocols in EPA guidance (EPA 1999, 73728). A modified Hess sampler was used and three locations were sampled and combined for a single composite site sample. The May 1997 sampling campaign included one site in Cañon de Valle below MDA P (Location ID 16-06711) and several reference streams. The June 2001 sampling campaign included the 1997 site (Location ID 16-06711) for Cañon de Valle and a site below the confluence with Burning Ground Spring.

# **3.3.5.2 Terrestrial System Sampling**

Adverse effects characterization for the terrestrial system used the characteristics of the small mammal populations in Cañon de Valle and the contaminant body burdens of small mammals as estimates for potential contaminant doses to the Mexican spotted owl (threatened and endangered species). Figure 3.3-10 shows the locations of the trapping arrays in Cañon de Valle and Pajarito Canyon (reference site).

Small mammal trapping was conducted in May 2001, September and October 2001, and May 2002. Two 5-ft-wide by 20-ft-long trapping grids were established in each canyon for the duration of the trapping events. A Sherman live trap and a pitfall trap occupied each grid location. The live traps were opened and baited and the pitfall traps uncovered in the late afternoons. Traps were checked and closed the following mornings. Newly captured individuals were identified, classified for reproductive status, ear tagged, and released. For the first two sampling periods, mark and recapture trapping was conducted for five days. These data are used to estimate population densities. After the population data were collected, individuals of prevalent species were collected for chemical analysis of whole animal contaminant body burdens. Individuals were analyzed for HE by EPA Method 8330 and TAL metals by EPA Method 6010B. The third sampling event consisted of trapping for body burden analysis only. Results of the mark and recapture trapping and the reproductive status classifications are presented in Appendix L and published in Bennett et al. (Bennett et al. 2002, 73796).

### **3.3.5.3 Deviations**

### Aquatic System Sampling

Two deviations were associated with the aquatic system sampling. The first deviation was that the results from the second round (September and October of 2001) of toxicity testing for sediment and site water were rejected because of high mortality in the laboratory control replicates. The acceptance criterion for the test is 70% average survival for the control replicates. The test had 72.5% average survival for the laboratory control with individual replicates ranging from 50% to 90%. In addition, the site sample survival results did not correspond to what is known about contamination in the sediment. Consequently, a decision was made with the High Performing Team to reject these data and repeat the sampling and analysis. An additional set of samples was collected in December 2002 (repeating the round 2 sampling) and the quality control (QC) data for these tests were acceptable. The baseline ecological risk assessment uses the results from the first and third rounds of toxicity testing to assess adverse effects.

The second deviation was for the benthic macro-invertebrate sampling in 2001. The Cerro Grande fire in 2000 resulted in substantial fire effects in the reference canyons used in the 1996 and 1997 benthic macro-invertebrate sampling. Flooding in those canyons after the fire resulted in changes to site conditions and the macro-invertebrate communities such that comparisons of Cañon de Valle to those sites was no longer useful. Consequently, the 2001 Cañon de Valle data were compared to the previous Cañon de Valle data and the two sites sampled in Cañon de Valle in 2001 were compared to each other. The absence of 2001 reference site data diminishes the evidence for associating changes in Cañon de Valle to the on-going drought.

### Terrestrial System Sampling

There were two deviations associated with the terrestrial sampling design. The body burden data associated with the fall 2001 sampling were rejected because of very large differences in constituent concentrations that are physiologically regulated, and are not contaminants. One example is a range of two orders of magnitude for calcium results. This difference points to an artifact in the sample preparation or the analysis. A third round of sampling was conducted in the spring of 2002 to collect additional small mammals for body burden analysis. These data were acceptable. The assessment of small mammal body burdens and potential dose to the Mexican spotted owl is based upon the analytical data from the first and third trapping periods.

The second deviation involves the species available for capture in the canyons. The sampling design was to capture individuals from multiple trophic levels, including shrews, which are insectivores. The literature indicates that insectivores often have the highest contaminant body burdens. Pitfall trapping was conducted in both canyons for shrews during the first two sampling rounds. None were captured. The absence of shrews is likely a consequence of the drought and the elimination of effluent support to the flow in Cañon de Valle. If shrews were present they would be an incidental prey species of the Mexican spotted owl given their rarity. The small mammals that were captured reflect the abundant species in the canyons and the likely prey species for owls hunting in those canyons. These species represent herbivore and omnivore trophic levels.

### **3.4 Results**

This section presents the results from surface water, alluvial groundwater, sediment, and ecorisk sampling programs. Each sampling program is described in terms of the number of samples collected and data quality issues concerning the sampling events. The results of the data quality assurance (QA)/QC assessments are presented in Appendix F. All analytical data are presented in Appendix G-3.

### **3.4.1 Data Results Overview**

# **3.4.1.1 Data Quality Assessment**

All analytical samples were sent for fixed-laboratory analysis at off-site commercial analytical laboratories. All analytical results received routine data validation, with some results receiving focused validation when appropriate. Validation results for all analytical data are summarized in Appendix F and indicate the dataset is of sufficient quantity and quality to be used in data analysis, including risk assessment.

# **3.4.1.2 Screening Methodology**

To identify which chemicals are COPCs for SWMU 16-021(c)-99, all chemicals detected in either SWMU 16-021(c)-99 sediment or water were subjected to a screening process. The screening process is described in section 1.5.

# **3.4.2 Analytical Data Presentation**

This section presents the analytical data results for surface water, alluvial groundwater, sediment, and ecological sampling results. A summary of all analytical data is provided in Appendix G-3.

# **3.4.2.1 Cañon de Valle Surface Water**

This section presents analytical and SP results from 1998 through 2002. The results are derived from three types of surface water sampling activities: (1) SP sampling, 2) quarterly sampling of surface water locations, and (3) surface water collected in support of ecotoxological testing. Sample locations are shown on Figure 3.3-2.

### **3.4.2.1.1 Cañon de Valle Surface Water: Evaluation of Inorganic Chemicals**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of all detected inorganic chemicals is provided in Table G-2.1 (located in Appendix G-2). This section includes the frequency of detected inorganic chemicals (Table 3.4-1); the screening results for inorganic chemicals that exceed the NMWQCC regulations numeric standard or other appropriate standard (Table 3.4-2); and the inorganic chemicals retained and eliminated as COPCs (Table 3.4-3).

To determine whether those chemicals that exceeded a screening standard are true contaminants present above naturally-occurring concentrations, a site-specific analysis was conducted using geochemistry. This analysis was also required due to a lack of an appropriate background water dataset. The importance of geochemical evaluations in distinguishing between contamination and naturally high background concentrations of elements has been recognized in the industry (EPA 1995, 76856; U.S. Navy 2002, 76854). One of the key processes considered in a geochemical evaluation of surface water is the effect of naturally-occurring suspended particulates on trace element concentrations. The most common suspended particulates in surface water samples are clay minerals, hydrous aluminum oxides, and aluminum hydroxides, hereafter referred to as "clays"; and iron oxide (Fe<sub>2</sub>O<sub>3</sub>), iron hydroxide [Fe(OH)3], and iron oxyhydroxide (FeO•OH) minerals, collectively referred to as "iron oxides." All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of approximately 1 mg/L indicate the presence of suspended clay minerals (Stumm and Morgan 1970, 76857; Hem 1985, 76855); higher aluminum concentrations is a qualitative indicator of the mass of suspended clay minerals. Iron also has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of approximately 1 mg/L under these conditions indicate the presence of suspended iron oxides (Hem 1985, 76855).

The analysis is conducted by plotting suspected contaminants against either aluminum or iron. For example, chromium is plotted against aluminum for naturally-occurring concentrations and site samples. If the naturally-occurring concentrations and site samples display a common linear trend, then it is most likely the elevated chromium concentrations are due to the presence of suspended clay minerals in the samples. The slope of a best-fit line through the points representing uncontaminated samples is equal to the average chromium/aluminum ratio. If some site samples are plotted above the trend established by the naturally-occurring concentrations samples, then those site samples have an anomalously high chromium/aluminum ratio, and most likely contain excess chromium that cannot be explained by these natural processes. Further details of the method are provided in Appendix I-2.

The results of the analysis conducted for Cañon de Valle surface water show that observed concentrations of aluminum, iron, lead, manganese, and silver that exceed a screening standard are the result of naturally-occurring concentrations.

Cañon de Valle surface water inorganic chemicals eliminated and retained for further consideration are listed in Table 3.4-3. Barium is the only COPC which consistently exceeds the screening standard at most locations. A brief description of each retained inorganic chemical with concentrations exceeding standards and the site-specific naturally-occurring concentration analysis is provided in Appendix I-4 and

Chemical	<b>Field</b> Preparation	Number of Analyses	Number of <b>Detects</b>	<b>Concentration Range</b> $(\mu g/L)$	<b>Percent Detected for 20</b> Samples or Greater <sup>a</sup>
Aluminum	Filtered	73	47	$[8.7]^{b}$ to 15000	80
	Unfiltered	84	79	[133] to 22700	
Antimony	Filtered	72	13	[0.14] to [33]	13
	Unfiltered	83	$\overline{7}$	$[0.08]$ to $[33]$	
Arsenic	Filtered	73	14	$[0.27]$ to $[5]$	24
	<b>Unfiltered</b>	84	23	[0.27] to 8.3	
<b>Barium</b>	Filtered	70	70	15.5 to 12900	100
	Unfiltered	81	81	16.8 to 16300	
Beryllium	Filtered	73	3	$[0.09]$ to $[4]$	16
	Unfiltered	84	22	$0.03$ to $[4]$	
<b>Boron</b>	Filtered	67	45	6.97 to [500]	67
	Unfiltered	74	50	3.06 to [500]	
Cadmium	Filtered	73	$\overline{7}$	$0.054$ to $[5]$	12
	Unfiltered	84	12	$[0.017]$ to $[2.6]$	
Calcium	Filtered	73	73	4200 to 43300	100
	Unfiltered	84	84	4290 to 44300	
Cesium	Filtered	$\overline{2}$	$\overline{2}$	700 to 800	$n/a^{\overline{c}}$
	Unfiltered	$\overline{2}$	$\overline{2}$	500 to 700	
Chloride	Filtered	9	9	4500 to 32000	100
	Unfiltered	67	67	200 to 39000	
Chromium	Filtered	73	40	[0.32] to 34.6	62
	Unfiltered	84	58	[0.38] to 24.3	
Cobalt	Filtered	73	39	$[0.23]$ to $[20]$	50
	Unfiltered	84	39	$[0.2]$ to $[20]$	
Copper	Filtered	73	28	[0.28] to 75.3	46
	Unfiltered	84	44	$[0.28]$ to 61.5	
Cyanide (Total)	Filtered	3	0	$[2.5 \text{ to } 10]$	n/a
	Unfiltered	3	$\mathbf 0$	$[2.5 \text{ to } 10]$	
Fluoride	Filtered	9	$\ensuremath{\mathsf{3}}$	100 to [1000]	75
	Unfiltered	67	54	$[14]$ to $[1000]$	
Iron	Filtered	73	45	13.3 to 10000	75
	Unfiltered	84	72	[64] to 17700	
Lead	Filtered	73	11	0.057 to 4.8	34
	Unfiltered	84	43	0.2 to 24.1	
Lithium	Filtered	3	$\mathsf 3$	3.5 to 18.1	n/a
	Unfiltered	3	$\mathsf 3$	6.2 to 25.8	
Magnesium	Filtered	73	73	1530 to 9590	100
	Unfiltered	84	84	1550 to 9580	
Manganese	Filtered	73	67	0.7 to 628	96
	Unfiltered	84	83	1.8 to 2290	

**Table 3.4-1 Frequency of Detected Inorganic Chemicals in Surface Water Samples from Cañon de Valle** 





*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br><sup>b</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$  n/a = Not applicable.

Chemical	Sample ID	Concentration Sample (1001)			NMWQCC Standard (Hôrl)	EPA MCL (µg/L)	Tap Water PRG EPA Region 6 (Tlên)	Screening Limit Exceeds
Aluminum	RE16-01-3231	Max. Detected Value	22700		$5000^{\mathrm{a,b}}$	50	$n/a^c$	Yes
	RE16-01-3132	Max. Undetected Value	589	$(U)^d$	$5000^{a,b}$	50	n/a	Yes
Antimony	RE16-99-3075	Max. Detected Value	6.4	$(J)^e$	n/a	6	n/a	Yes
	RE16-98-3112	Max. Undetected Value	33	(U)	n/a	6	n/a	Yes
Arsenic	RE16-98-3021	Max. Detected Value	8.3	(J)	100 <sup>f</sup>	10	n/a	No
	RE16-01-3278	Max. Undetected Value	5	(U)	100 <sup>f</sup>	10	n/a	No
<b>Barium</b>	RE16-01-3072	Max. Detected Value	16300		1000 <sup>f</sup>	2000	n/a	Yes
Beryllium	RE16-00-3141	Max. Detected Value	1.3	(J)	n/a	4	n/a	No
	RE16-00-3131	Max. Undetected Value	4	(U)	n/a	4	n/a	No
Boron	RE16-00-3163	Max. Detected Value	69.2	(J)	$750^a$	na <sup>9</sup>	n/a	<b>No</b>
	RE16-00-3132	Max. Undetected Value	500	(U)	750 <sup>a</sup>	na	n/a	No
Cadmium	RE16-00-3268	Max. Detected Value	1.6	(J)	$10^{\text{f}}$	5	n/a	No
	RE16-00-3316	Max. Undetected Value	5	(U)	$10^{\text{f}}$	5	n/a	No
Calcium	RE16-00-3163	Max. Detected Value	44300		na	na	na	na
Cesium	RE16-98-3018	Max. Detected Value	800		na	na	na	na
Chloride	RE16-99-3199	Max. Detected Value	39000		250000 <sup>h</sup>	250000	n/a	No
Chromium	RE16-99-3047	Max. Detected Value	34.6		$50^{\dagger}$	100	n/a	No
	RE16-98-3020	Max. Undetected Value	5.9	(U)	$50^{\text{f}}$	100	n/a	No
Cobalt	RE16-98-3021	Max. Detected Value	12.9	(J)	50 <sup>a</sup>	na	n/a	No
	RE16-00-3131	Max. Undetected Value	20	(U)	50 <sup>a</sup>	na	n/a	No
Copper	RE16-01-3250	Max. Detected Value	75.3		$500^{\rm b}$	1000	n/a	No
	RE16-01-3152	Max. Undetected Value	15.3 $(U)$		500 <sup>b</sup>	1000	n/a	No
Fluoride	RE16-00-3163	Max. Detected Value	432		1600 <sup>f</sup>	2000	n/a	No
	RE16-98-3107	Max. Undetected Value	1000	(U)	1600 <sup>f</sup>	2000	n/a	No
Iron	RE16-98-3021	Max. Detected Value	17700		1000 <sup>h</sup>	300	n/a	Yes
	RE16-01-3150	Max. Undetected Value	406	(U)	1000 <sup>h</sup>	300	n/a	Yes
Lead	RE16-01-3072	Max. Detected Value	24.1		$50^{\dagger}$	15	n/a	Yes
	RE16-98-3107	Max. Undetected Value		4.2 $(U)$	$50^{\dagger}$	15	n/a	No
Lithium	RE16-98-3021	Max. Detected Value	25.8		na	na	730	No

**Table 3.4-2 Screening of Inorganic Chemicals Detected in Cañon de Valle Surface Water Samples** 

**Table 3.4-2 (continued)** 

Chemical	Sample ID	Concentration Sample (Tien)	NMWQCC Standard (µg/L)	EPA MCL (µg/L)	Tap Water PRG (µg/L) EPA Region 6	Screening Limit Exceeds		
Magnesium	RE16-00-3164	Max. Detected Value	9590		na	na	na	na
Manganese	RE16-98-3081	Max. Detected Value	2290		200 <sup>h</sup>	50	n/a	Yes
	RE16-98-3114	Max. Undetected Value	8.8	(U)	200 <sup>h</sup>	50	n/a	No
Mercury	RE16-01-3154	Max. Detected Value	0.97		$0.77$ <sup>1</sup>	$\overline{2}$	n/a	Yes
	RE16-01-3080	Max. Undetected Value	$\mathbf 1$	(U)	$0.77^{i}$	$\overline{2}$	n/a	Yes
Molybdenum	RE16-98-3021	Max. Detected Value	6.3	(J)	$1000^a$	na	n/a	No
	RE16-98-3044	Max. Undetected Value	4.9	(U)	1000 <sup>a</sup>	na	n/a	No
Nickel	RE16-01-3231	Max. Detected Value	13.2	(J)	$200^a$	na	n/a	No
	RE16-00-3132	Max. Undetected Value	40	(U)	$200^a$	na	n/a	No
Nitrate	RE16-98-3018	Max. Detected Value	900		$10000^T$	10000	n/a	No
	RE16-98-3020	Max. Undetected Value	200	(U)	10000 <sup>†</sup>	10000	n/a	No
Nitrate-Nitrite	RE16-01-3130	Max. Detected Value	49200		10000 <sup>t</sup>	na	n/a	Yes
as N	RE16-00-3313	Max. Undetected Value	1110	(U)	10000 <sup>f</sup>	na	n/a	No
Perchlorate	RE16-00-3133	Max. Detected Value	17.1		$4^{j}$	na	n/a	Yes
	RE16-00-3150	Max. Undetected Value	20	(U)	$4^{\mathsf{J}}$	na	n/a	Yes
Potassium	RE16-00-3163	Max. Detected Value	11000		na	na	na	na
	RE16-01-3196	Max. Undetected Value	2330	(U)	na	na	na	na
Selenium	RE16-01-3280	Max. Detected Value	5.33		$5^{\prime}$	50	n/a	Yes
	RE16-02-45961	Max. Undetected Value	5	(U)	$5^{\mathsf{i}}$	50	n/a	No
Silver	RE16-98-3081	Max. Detected Value	1380		$50^{\text{f}}$	100	n/a	Yes
	RE16-00-3131	Max. Undetected Value	10	(U)	$50^{\dagger}$	100	n/a	No
Sodium	RE16-00-3208	Max. Detected Value	26200		na	na	na	na
Strontium	RE16-98-3019	Max. Detected Value	133		na	na	22000	No
Sulfate	RE16-00-3133	Max. Detected Value	31700		$\frac{600000^{\overline{h}}}{2}$	250000	n/a	No
Thallium	RE16-98-3083	Max. Detected Value	5.9	(J)	n/a	$\overline{2}$	n/a	Yes
	RE16-99-3023	Max. Undetected Value	5.6	(U)	n/a	$\overline{2}$	n/a	Yes
Uranium	RE16-00-3163	Max. Detected Value	1.91		5000 <sup>†</sup>	30	n/a	No
	RE16-98-3044	Max. Undetected Value	126	(U)	5000 <sup>†</sup>	30	n/a	Yes
Vanadium	RE16-98-3021	Max. Detected Value	33.1	(J)	100 <sup>b</sup>	na	n/a	No.
	RE16-00-3132	Max. Undetected Value	10 <sup>1</sup>	(U)	100 <sup>b</sup>	na	n/a	No
Zinc	RE16-02-45961	Max. Detected Value	100		10000 <sup>h</sup>	5000	n/a	No
	RE16-00-3207	Max. Undetected Value	38.1	(U)	10000 <sup>h</sup>	5000	n/a	No

### **Table 3.4-2 (continued)**

Sources: 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867; and California DHS 2003, 76862.

- a NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).<br> $^{b}_{2}$  NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103).
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 $d^n$ <br>  $e^{n/a}$  = Not applicable.<br>  $e^{n/a}$  = The chemical is classified "undetected."<br>  $f^{(1)}$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.<br>  $g^{($ 

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#### **Table 3.4-3**

#### **Retained and Eliminated Inorganic Chemicals in Cañon de Valle Surface Water Samples**





# **Table 3.4-3 (continued)**

includes maximum concentrations detected, relevant locations where the chemical has been detected, and the dates of detection.

# **3.4.2.1.2 Cañon de Valle Surface Water: Evaluation of Organic Chemicals**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of all detected organic chemicals is provided in Table G-2.2 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-4), the screening results for organic chemicals, which exceed the NMWQCC regulations numeric standard or other appropriate standard (Table 3.4-5), and the retained and eliminated organic chemicals (Table 3.4-6). Retained HE compounds include dinitrosodimethylamine (DNX), mononitrosodimethylamine (MNX), RDX, and TNT, however, RDX is the most prevalent HE COPC. Low concentrations (ppb) of tetrachloroethene and trichloroethene were also detected and retained as COPCs. A brief description of the retained organic COPCs with concentrations exceeding screening standards is provided in Appendix I-4.

# **3.4.2.1.3 Cañon de Valle Surface Water: Evaluation of Tritium**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of the detected tritium in surface water samples collected in Cañon de Valle is provided in Table G-2.3 (located in Appendix G-2). Tritium was the only radionuclide detected in Cañon de Valle surface water. The frequency of detected of tritium (Table 3.4-7), the screening results (Table 3.4-8), and the retained and eliminated analysis (Table 3.4-9) are presented in this section. The results show that tritium was not present above either the EPA MCL or the NMWQCC regulations numeric standard.





*Source:* EPA 1989, 08021.<br>a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.<br>by tables in headacts are halowed that the limits afthrown agency beneficting

ັ Values in brackets are below detection limits, although some chemicals may be detected at values within this range.<br><sup>c</sup> n/a = Not applicable.<br><sup>d</sup> DNX = Hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine.

 $e$  HMX = Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

 $\int_{0}^{f}$  MNX = Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine. <sup>t</sup> MNX = Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine.<br> $\frac{g}{g}$ RDX = Hexahydro-1,3,5-trinitro-1,3,5-triazine.

 $h_{\text{TNX}} = H_{\text{exahydro-1,3,5-trinitroso-1,3,5-triazine}}$ .





g(EPA 2002, 76866).

**Table 3.4-6 Retained and Eliminated Organic Chemicals in Cañon de Valle Surface Water Samples** 

Chemical	Retained/ <b>Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Acetone	Eliminated	No values above screening limit.
Amino-2,6-dinitrotoluene[4-]	Eliminated	No values above screening limit.
Amino-4,6-dinitrotoluene[2-]	Eliminated	No values above screening limit.
Amino-x,6-dinitrotoluene[x-]	Eliminated	No values above screening limit.
Bis(2-ethylhexyl)phthalate	<b>Retained</b>	Detection limit exceeds screening limit.
Butanone[2-]	Eliminated	No values above screening limit.
Dichloroethene[cis-1,2-]	Eliminated	No values above screening limit.
<b>DNX</b>	<b>Retained</b>	Maximum value exceeds screening limit.
<b>HMX</b>	Eliminated	No values above screening limit.
Methylene Chloride	<b>Retained</b>	Less than 5% of analyses result in a detection but the detection limit exceeds the screening limit.
<b>MNX</b>	<b>Retained</b>	Maximum value exceeds screening limit.
Naphthalene	Eliminated	Greater than 20 analyses were taken and the number of detected values comprise less than 5% of the total number of analyses.
Nitroglycerin	<b>Retained</b>	Less than 5% of analyses result in a detection but the detection limit exceeds the screening limit.
Nitrotoluene[2-]	Eliminated	Greater than 20 analyses were taken and the number of detected values comprise less than 5% of the total number of analyses.
<b>RDX</b>	<b>Retained</b>	Maximum value exceeds screening limit.
Tetrachloroethene	<b>Retained</b>	Maximum value exceeds screening limit.
<b>TNX</b>	Eliminated	No values above screening limit.
Trichloro-1,2,2-trifluoroethane[1,1,2-]	Eliminated	Greater than 20 analyses were taken and the number of detected values comprise less than 5% of the total number of analyses.
Trichlorobenzene[1,2,3-]	Eliminated	No values above screening limit.
Trichloroethene	<b>Retained</b>	Maximum value exceeds screening limit.
Trinitrobenzene[1,3,5-]	Eliminated	Greater than 20 analyses were taken and the number of detected values comprise less than 5% of the total number of analyses.
Trinitrotoluene[2,4,6-]	<b>Retained</b>	Maximum value exceeds screening limit.

<b>Chemical</b>	Field	Number of	Number of	<b>Concentration Range</b>	<b>Percent Detected for 20</b>
	<b>Preparation</b>	<b>Analyses</b>	<b>Detects</b>	(pCi/L)	<b>Samples or Greater</b> <sup>a</sup>
Tritium	Jnfiltered	26	23	$[2.9]$ <sup>p</sup> to 167.36	88

**Table 3.4-7 Frequency of Detected Tritium in Cañon de Valle Surface Water Samples** 

*Source:* EPA 1989, 08021.

a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b<br>Values in brackets are below detection limits, although some chemicals may be detected at values within this range.





Sources: 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900,"Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; and EPA 2003, 76867.

a<br>NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $b$  n/a = Not applicable.

 $\rm ^c$  (U) = The chemical is classified "undetected."





### **3.4.2.1.4 Cañon de Valle Surface Water: Flow Rate and Water Chemistry**

This subsection presents the screening data results for discharge, conductivity, pH, stable isotopes, and temperature data collected during the SP measurements between 1998 and 2002.

#### Discharge Results

Figure 3.4-1 shows the discharge measurements for each SP location for Cañon de Valle. The locations of the SPs where discharge measurements were conducted are shown on Figure 3.3-2. The following section summarizes the observed trends from the 13 discharge events:



**Figure 3.4-1. Discharge results for stream discharge events measured between June 1998 and**  Discharge results for stream discharge events measured between June 1998 and August 2002 **August 2002** Figure 3.4-1.

- 1. The channel is usually dry upstream from SP#4 (Peter Seep foot).
- 2. Discharge from SWSC Spring (when running) contributes to the first gaining portion of the channel.
- 3. The channel loses water between the SWSC Spring confluence and Burning Ground Spring confluence.
- 4. During the investigation period, the perennial reach of Cañon de Valle in TA-16 is approximately 1900 ft long, beginning at the confluence with Burning Ground Spring and ending between SP#10 and SP#11, just downstream of MDA P.
- 5. The channel loses from Burning Ground Spring to SP#12. In particular, the broad canyon bottom area between SP #9 and SP #10 generally loses, and during low flow periods the water in the channel consistently goes subsurface within 90 ft of SP#10.
- 6. An unnamed seep is present adjacent to Well 16-02659 located approximately 3500 ft downstream of the 260 outfall. Based on data shown in Figure 3.4-1, this location also shows a noticeable water input, which may be the result of a subsurface source related to the seep. Noticeable temperature and pH changes were recorded at this location during the Fall 2000 profile. Moreover, chemical trend data for barium indicate a barium input occurs at this location (see section 3.5).
- 7. Of the 13 discharge events, 2 were measured during the spring following a heavy snow year. These 2 discharge profiles recorded the highest discharge and show some exceptions to the general observations. These exceptions include: a gaining reach between SP#8 and SP#10 and measurable flow upchannel of the 260 outfall. This may explain why the highest contaminant concentrations were also observed during the snowmelt runoff.

### Conductivity Results

Conductivity measurements presented in Figure 3.4-2 generally show a steady to slightly increasing trend downstream, with the November 2000, March 2001, and October 2001 SPs showing the largest variation with distance. All of these profiles were collected during wet periods.

### Temperature and pH Results

Temperature profiles shown in Figure 3.4-3 show a general downward trend with distance from the 260 outfall. A notable variation occurs approximately 3500 ft downstream from the 260 outfall near Well 16-02659. The temperature results (i.e., slight increase) support the presence of an alluvial input at this location. Seasonal changes (both fall and winter), when present, deviate toward a common temperature, indicative of a subsurface water source or seep near Well 16-02659. The variability of the temperature change at this location may result from thermal mixing and the differences in flow rate, caused by precipitation, between the subsurface input and surface water.

Cañon de Valle surface water pH measurements are shown in Figure 3.4-4. Despite considerable scatter in the data, in general, a pH change is observed in the same location where changes in temperature and conductivity are also observed, indicating a subsurface input to the surface water at this location.











### Seep Dynamics

The location of the head and foot of Peter Seep was not dynamic during the investigation period. The 2001 snowmelt season and the fall of 2001 were the only times water was observed at the Peter Seep 'head', approximately 500 ft up channel from the 260 outfall confluence. at other times, water was observed to originate from the 'foot'. For data analysis purposes, seep data are compiled with the surface water data.

### Stable Isotopes

Surface water samples were analyzed for  $\delta^{18}$ O and  $\delta$ D at the headwaters of Cañon de Valle, at the confluence of Cañon de Valle and the Fishladder drainage, at the confluence of Cañon de Valle and Water Canyon, and at Peter Seep (Figure 3.4-5). The δD data are not shown because they show behavior similar to the  $\delta^{18}$ O data. The headwaters have the most negative values because the headwater area is the highest elevation site sampled. Compared to the alluvial groundwater (e.g., Well 16-02657, see Figure 3.4-9), surface water does not always follow the same trends, indicating there are differences between surface and alluvial groundwater (even though there is exchange between the two). Similar differences are seen between the contaminant chemistry of surface water and alluvial groundwater (see section 5.2).

Nitrogen isotopes ( $\delta^{15}$ N) were examined as a possible way of identifying natural versus contaminant sources of nitrate and to identify whether there was active denitrification at TA-16. With regard to natural versus contaminant sources, the  $\delta^{15}$ N data are ambiguous and thus did not turn out to be diagnostic. However, with regard to denitrification, there appears to be a correlation between nitrate concentrations and  $\delta^{15}$ N in the waters of Canon de Valle, where larger values of  $\delta^{15}$ N correspond to higher concentrations of nitrate (Figure 3.4-6). This correlation indicates that denitrification is occurring because one of the characteristics of denitrification is an increase in  $\delta^{15}$ N. Additional evidence and discussion of nitrate degradation is presented in section 5.0.

Tritium concentrations in surface water are shown in Figure 3.4-7. The locations show no clear trends except that the Cañon de Valle headwaters tend to have the lowest tritium concentrations. This suggests that the headwaters are less affected by Laboratory atmospheric releases. The relatively high levels of tritium, although not a risk driver, suggest that the water in the alluvial aquifer is relatively young (less than a few decades), or has a large young water component. These results are similar to values for the alluvial wells (see Well 16-02658 example on Figure 3.4-7). However, the surface waters have a wider range of values, probably because the alluvial system is more mixed than the surface water.

# **3.4.2.1.5 Cañon de Valle Geophysical Studies**

Geophysics conducted at the site in support of the Phase III RFI consisted of three field efforts conducted in 1999, 2000, and 2002. The 1999 results demonstrated the capability of HRR as a nonintrusive means to detect and characterize subsurface moisture conditions. The 2001 survey was a more broad continuation of that effort. Line locations are shown on Figure 3.3-6. In September 2002, CSAMT and NSAMT geophysical survey work was performed. Line locations are provided on Figure 3.3-7. Figure 3.4-8 shows the HRR results for a line located within the Cañon de Valle. Complete results from all geophysical surveys are included in Appendix D.


**Figure 3.4-5. Plot of** δ**18O from surface water samples from Cañon de Valle** 



**Figure 3.4-6. Nitrogen isotopes (**δ**15N) and nitrate concentrations in Cañon de Valle waters.** 



**Figure 3-4-7. Tritium concentrations in TA-16 area surface water and Well 16-02658 groundwater** 



The important highlights of the surveys that influence conceptual model development were:

- 1. At the subsurface of the Burning Ground Spring wetland area, there is a conductive region implying possible subsurface water infiltration at this location (deeper than alluvium).
- 2. The area approximately 200 ft upstream from MDA P shows an approximately 20-ft-thick low resistance layer dipping to the west. Just downstream of MDA P the surface water flow rate decreases, indicating a loss zone as discussed earlier in the SP discharge results.
- 3. Further downstream from MDA P, the 2-D longitudinal line shows laterally discontinuous zones of low resistance; these zones could represent saturated zones of alluvial groundwater. This conductive region does not show up in the cross sectional line at SP#16. It is possible that there were unsaturated conditions at that location at the time of measurement.
- 4. The deep conductive horizons observed in the CSAMT and NSAMT inversion models extend below the 6400-ft elevation. Information from several intermediate-depth wells indicates a regional water table near the 1200-ft depth in the vicinity of Regional Aquifer Well CdV R-37-2. It is possible that the water table elevation in the TA-16 area may range from 5800 to 6400 ft. These are the elevations where the CSAMT and NSAMT inversion models identify anomalously conductive features.

# **3.4.2.2 Cañon de Valle Alluvial Groundwater**

Laboratory analyses and water level, conductivity, and temperature screening results for quarterly groundwater sampling conducted between 1998 and 2002 are described below in detail. Complete time series charts for the alluvial wells are included in Appendix H. Sample locations are shown on Figure 3.3-2. A summary of all samples submitted for laboratory analyses is provided in Appendix G-1. A summary of all analytical results is provided in Appendix G-3.

## **3.4.2.2.1 Cañon de Valle Alluvial Groundwater: Evaluation of Inorganic Chemicals**

A summary of all detected inorganic chemicals is provided in Table G-2.4 (located in Appendix G-2). This section includes the frequency of detected inorganic chemicals (Table 3.4-10); screening results for inorganic chemicals that exceed the NMWQCC regulations numeric standards, or other appropriate standard (Table 3.4-11); and the chemicals retained and eliminated as COPCs (Table 3.4-12). In developing the final retained and eliminated table, a site-specific naturally-occurring concentration analysis was conducted using geochemistry. Further details of this analysis are provided in Appendix I-2. This analysis showed the detected concentrations of aluminum, arsenic, beryllium, chromium, iron, lead, selenium, uranium, and vanadium were the result of naturally-occurring concentrations. The screening results (Table 3.4-12) include the results of the geochemical evaluation for alluvial groundwater in Cañon de Valle. Barium and manganese are the most prevalent COPCs in the Cañon de Valle alluvial groundwater. A brief description of retained inorganic COPCs with concentrations exceeding standards is provided in Appendix I-4.

## **3.4.2.2.2 Cañon de Valle Alluvial Groundwater: Evaluation of Organic Chemicals**

A summary of all detected organic chemicals is provided in Table G-2.5 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-13); screening results for organic chemicals that exceed the NMWQCC regulations numeric standards, or other appropriate standard







# **Table 3.4-10 (continued)**



### **Table 3.4-10 (continued)**

*Source:* EPA 1989, 08021.

a<br>The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br><sup>D</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$ <sub>n/a</sub> = Not applicable.



# **Table 3.4-11**

## **Screening of Inorganic Chemicals Detected in Cañon de Valle Alluvial Groundwater Samples**

# **Table 3.4-11 (continued)**



**Table 3.4-11 (continued)** 

Chemical	Sample ID	Sample Concentration (Hârl)			NMWQCC Standard (µg/L)	EPA MCL (µg/L)	Tap Water PRG EPA Region 6 (Hârl)	Screening Limit <b>Exceeds</b>
Nitrate-Nitrite	RE16-00-3299	Max. Detected Value	7330		10000 <sup>f</sup>	na	n/a	No
as N	RE16-01-3007	Max. Undetected Value	1000	(U)	$10000$ <sup>f</sup>	na	n/a	No
Perchlorate	RE16-00-3117	Max. Detected Value	19.1		$4^{j}$	na	n/a	Yes
	RE16-01-3001	Max. Undetected Value	4.79	(U)	$4^{j}$	na	n/a	Yes
Potassium	RE16-00-3299	Max. Detected Value	22100		na	na	na	na
	RE16-98-3037	Max. Undetected Value	5000	(U)	na	na	na	na
Rubidium	RE16-98-3006	Max. Detected Value	900		na	na	na	na
	RE16-98-3005	Max. Undetected Value	50	(U)	na	na	na	na
Selenium	RE16-01-3001	Max. Detected Value	14		$5^{\mathsf{i}}$	50	n/a	Yes
	RE16-00-3117	Max. Undetected Value	8	$(UJ)^k$	$5^{\mathsf{i}}$	50	n/a	Yes
Silver	RE16-01-3001	Max. Detected Value	8.4	(J)	$50^{\circ}$	100	n/a	No
	RE16-98-3037	Max. Undetected Value	10	(U)	$50^{\circ}$	100	n/a	No
Sodium	RE16-01-3161	Max. Detected Value	146000		na	na	na	na
	RE16-98-3035	Max. Undetected Value	17000	(U)	na	na	na	na
Strontium	RE16-98-3007	Max. Detected Value	220		na	na	22000	No
Sulfate	RE16-01-3100	Max. Detected Value	109000		600000 <sup>h</sup>	250000	n/a	No
Thallium	RE16-98-3030	Max. Detected Value	7.6	(J)	n/a	$\overline{2}$	n/a	Yes
	RE16-98-3000	Max. Undetected Value	9.1	(U)	n/a	$\overline{2}$	n/a	Yes
Uranium	RE16-00-3117	Max. Detected Value	8.38		5000 <sup>f</sup>	30	n/a	No
	RE16-98-3030	Max. Undetected Value	126	(U)	5000 <sup>f</sup>	30	n/a	Yes
Vanadium	RE16-00-3299	Max. Detected Value	132		100 <sup>b</sup>	na	n/a	Yes
	RE16-01-3164	Max. Undetected Value	12.3	(U)	100 <sup>b</sup>	na	n/a	No
Zinc	RE16-99-3034	Max. Detected Value	1840		10000 <sup>h</sup>	5000	n/a	No
	RE16-00-3238	Max. Undetected Value	189	(U)	10000 <sup>h</sup>	5000	n/a	No

Sources: 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867; and California DHS 2003, 76862.

a<br>
NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3.3103).

b<br>b NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $\frac{c}{n/a}$  = Not applicable.

 $d$  (U) = The chemical is classified "undetected."

e (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain that usual.

f<br>MMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

## **Table 3.4-11 (continued)**

 $9$  na = Not available.

h<br>NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

i<br>NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900).

j California DHS 2003, 76862.

k (UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain that usual.

# **Table 3.4-12**

# **Retained and Eliminated Inorganic Chemicals in Cañon de Valle Alluvial Groundwater Samples**





# **Table 3.4-12 (continued)**

### **Table 3.4-13**

# **Frequency of Detected Organic Chemicals in Cañon de Valle Alluvial Groundwater Samples**





# **Table 3.4-13 (continued)**

*Source:* EPA 1989, 08021.

a<br>The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br><sup>D</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

c<br>n/a = Not applicable.

(Table 3.4-14); and the chemicals retained and eliminated as COPCs (Table 3.4-15). RDX is the dominant COPC in Cañon de Valle alluvial groundwater and is detected throughout the canyon. A brief description of the retained organic COPCs with concentrations exceeding standards is provided in Appendix I-4.

### **3.4.2.2.3 Cañon de Valle Alluvial Groundwater: Evaluation of Tritium**

Cañon de Valle alluvial groundwater samples were analyzed for tritium. A summary of all detected tritium is provided in Table G-2.6 (located in Appendix G-2). The frequency of detected tritium is provided in Table 3.4-16. Screening results for tritium are provided in Table 3.4-17, and the retained and eliminated analysis are presented in Table 3.4-18. The results show tritium was not present above either the EPA MCL or the NMWQCC regulations numeric standard.

### **3.4.2.2.4 Cañon de Valle Alluvial Groundwater: Well Level, Water Chemistry, Precipitation, and Seep Dynamics**

Complete graphical summaries and electronic data for the alluvial well measurements are included in Appendix H. A brief summary of the screening measurements follows.

#### Well 16-02655

This well is located in the upland or mesa top area west of TA-16 building 260 (Figure 3.3-2). Water levels in this well were very dynamic, showing as much as a 5-ft increase in water level following the spring 2001 snowmelt. There was no static saturated thickness in this well (typically dry). There does appear to be storage of water in the alluvial area surrounding the well, and the well responded to sustained rainfall input in the fall of 2000. Temperature results show annual fluctuations between 4 and 15°C. Conductivity measurements were only recorded while the well was wet. There is no consistent trend associated with the conductivity values.

#### Well 16-02656

Well 16-02656 is located upstream of Peter Seep and the 260 outfall near the base of MDA R (Figure 3.3- 2). Water levels in Well 16-02656 show distinct responses to both rainfall and snowmelt inputs. There is an approximate saturated thickness of 3 ft in this well; following the snowmelt of spring 2001, saturated thickness increased by 2 ft. Temperature measurements had an annual variation between 5 and 12°C. Conductivity values ranged between 0.200 and 0.400 µS/cm. However, there were slight increases in conductivity following rainfall inputs during the summer of 2000 and 2001.

#### Well 16-02657

Well 16-02657 is located downstream of the 260 outfall (Figure 3.3-2). It was not equipped with an automated datalogger because the well is frequently dry. Screening results from the manual measurements taken during monthly monitoring and quarterly sampling show similar temperature variations to Well 16-02656. The saturated thickness is approximately 0.5 ft. During the summer of 1998 and snowmelt of 2001, the saturated thickness increased to approximately 4 ft. There are no consistent conductivity trends.



 $\overline{\mathbf{C}}$ Ė ś Š é Table 3.4-14 م<br>موج ैः<br>र l, Č Ā  $\mathsf{C}$  $\ddot{\phantom{0}}$ 

J.



**Table 3.4-14 (continued)**  Table 3.4-14 (continued)  $\overline{S}$ 

Sources: 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900; "Standards applicable to attainable or Sources: 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900; "Standards applicable to attainable or<br>designated uses unless otherwise specified in 20.6 designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; and EPA 2003, 76867.

RE16-01-3066 Max. Detected Value 46.6 na na 2.2 Yes Trinitrotoluene[2,4,6-]

46.6  $\tilde{\omega}$ 

Yes

Γã <u>ლ</u>

na ma

Yes

 $2.2$ 

RE16-00-3117 Max. Undetected Value 13 (U) na na 13 anis 13 Aes

 $\widehat{=}$ 

Max. Undetected Value

RE16-00-3117

a<sub>na</sub> = Not available. na = Not available.  $b(U)$  = The chemical is classified "not detected."  $P(U)$  = The chemical is classified "not detected."

c(J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

 $d_{\text{n/a}}$  = Not applicable. n/a = Not applicable.

e (UJ) = The chemical is classified "not detected" with an expectation that the reported result is more uncertain than usual. (UJ) = The chemical is classified "not detected" with an expectation that the reported result is more uncertain than usual. f NMWQCC Groundwater Human Health Standards (20 NMAC 6.2.3103).NMVQCC Groundwater Human Health Standards (20 NMAC 6.2.3103)

## **Table 3.4-15 Retained and Eliminated Organic Chemicals in Cañon de Valle Alluvial Groundwater Samples**



### **Table 3.4-16 Frequency of Detected Tritium in Cañon de Valle Alluvial Groundwater Samples**



*Source:* EPA 1989, 08021.<br>a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br><sup>b</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.





*Sources:* 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through<br>20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; and EPA 2003, 76867.

<sup>a</sup> NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $<sup>b</sup>$  n/a = Not applicable.</sup>

 $\rm ^c$  (U) = The chemical is classified as "undetected."

# **Table 3.4-18 Retained and Eliminated Tritium for Cañon de Valle Alluvial Groundwater Samples**



#### Well 16-02658

Well 16-02658 is located within the middle reach of the canyon bottom and downstream of SWSC and Burning Ground Springs (Figure 3.3-2). Over the study period, this mid-canyon well was the least dynamic. Following the spring 2001 snowmelt, there was an approximately a 0.5-ft increase in saturated thickness. There is not clear evidence of rainfall input at this location. The saturated thickness was approximately 4 ft. The stability in measured saturated thickness may be due to the well proximity to Burning Ground Spring, or more storage potential in the alluvium because the cross-sectional area of the channel is greater than at other locations within the canyon. Annually, the temperature fluctuated between 3 and 13°C. Conductivity ranges from approximately 0.200 to 0.300 µS/cm.

#### Well 16-02659

Well 16-02659 is located in the lower reach of the canyon bottom downstream from MDA P (Figure 3.3-2). Saturated thickness measured in this well showed summer and fall rainfall inputs and spring 2001 snowmelt inputs. The spring 2001 snowmelt increased the saturated thickness in this well (which is typically at 2 ft) by more than 2 ft. Annually, the temperature fluctuated between 2 and 13°C. Conductivity ranged from approximately 0.200 to 0.300 µS/cm.

#### Stable Isotope Results

Stable isotope samples ( $\delta^{18}$ O,  $\delta$ D, and  $\delta^{15}$ N) were collected from alluvial groundwater at TA-16 in order to better understand differences in hydrologic and geochemical responses at various canyon and mesa locations. Comparisons of the Cañon de Valle and TA-16 mesa alluvial groundwater isotopic

compositions are shown in Figures 3.4-9 and 3.4-10. The data for Well 16-02655 are distinctive from the other wells in that they have substantially fewer negative  $\delta^{18}$ O and  $\delta$ D values. Well 16-02655 is located on the mesa top in the steam plant drainage (Figure 3.3-2), while the other wells are located in Cañon de Valle. This difference in isotopic compositions probably occurs because it is likely water that enters Well 16-02655 originates from local precipitation and snowmelt on the mesa top, whereas water in the Cañon de Valle wells is at least partially derived from spring flow, which is recharged at higher elevations (see section 4.0) and possibly from higher elevation runoff. The Cañon de Valle wells all show strong seasonal responses, wherein isotopic compositions generally peak at approximately –10.75 permil (from summer rains) and valley at less than  $-11.5$  permil (from cold season precipitation). However, the peaks and valleys are not of the same magnitude and do not occur at the same time. This inconsistent behavior is similar to that observed for water level changes (see section 3.4.2.2.4) and reduction/oxidation chemistry, indicating the Cañon de Valle alluvial system is not homogenous.

In Figure 3.4-10, the solid line is the local meteoric water line (Vuataz and Goff 1986, 40083). Precipitation data are plotted on or near the meteoric water line. Large deviations to the right of the line indicate evaporation after precipitation reaches the ground. These data show little to no post-precipitation event evaporation effects.

A limited amount of  $\delta^{18}$ O and  $\delta$ D data has been collected from alluvial well samples in Martin Spring Canyon (Well 16-06293, Well 16-06294, and Well 16-06295) and these data are plotted with the Cañon de Valle well data in Figure 3.4-11 (Well 16-02657, Well 16-02658, and Well 16-02659). Although there is some overlap, the Martin Spring Canyon wells all tend to have fewer negative isotopic values than the Cañon de Valle wells. This observation is consistent with the isotopic data from the TA-16 springs (see section 4.4.2.1.7); as that Martin Spring has distinctly fewer negative isotopic values than Burning Ground and SWSC Springs in Cañon de Valle.

In Figure 3.4-11, the solid line is the local meteoric water line (Vuataz and Goff 1986, 40083). Precipitation data are plotted on or near the meteoric water line. Large deviations to the right of the line indicate evaporation after precipitation reaches the ground. These data show little to no post-precipitation event evaporation effects. With regard to natural versus contaminant sources, the  $\delta^{15}$ N data are ambiguous and thus did not turn out to be diagnostic (see section 3.4.2.1.4).

Tritium concentrations in alluvial water are shown in Figure 3.4-12. There is similarity in the general trends between the wells that reflect variations in atmospheric tritium input and mixing between different water sources or recharge pathways. However, there are notable differences in tritium concentrations between some of the wells. These differences are an indicator of the heterogeneity in the alluvial groundwater system and also reflect the different inputs of water along the canyon. The relatively high levels of tritium, although not a risk driver, suggest that the water in the alluvial groundwater is relatively young (less than a few decades), or has a large young water component. These results are similar to values for surface water discussed earlier in section 3.0 and show the same main peaks and valleys as the springs tritium data discussed in section 4.0.

## Reduction/Oxidation Chemistry

Because the Cañon de Valle alluvial groundwater and surface water systems are interconnected and are the focus of risk assessment and possible remediation, investigations were conducted to characterize the geochemical conditions in the canyon bottom, particularly the redox (reducing or oxidizing) conditions in the alluvial aquifer. The redox state of the alluvial aquifer can control the speciation and mobility of metals, and the degradation of contaminants such as nitrate and the various HE compounds. The redox



### **Figure 3.4-9. Comparison of** δ**18O data from shallow wells in Cañon de Valle and on the TA-16 Mesa**

**EX2003-0480 EREX 11/2002 1/2002 1/2002 1/2002 1/2002 1/2002 1/2003 3/2002 2003** conditions focused on the alluvial system because higher contaminant concentrations typically exist in the alluvial aquifer rather than in the surface water system, and lower flow rates allow more time for geochemical and biogeochemical reactions to occur. Plots of redox-sensitive analytes (aluminum, iron, nitrate, and sulphate) suggest that redox conditions in the aquifer vary with time and distance along the canyon, which is consistent with a more detailed study of Jemez alluvial aquifer redox conditions (Groffman and Crossey 1999, 76859). Well 16-02657 is near the 260 outfall, Well 16-02658 is situated downcanyon just below Burning Ground Spring and Well 16-02659 is below MDA P (Figure 3.3-2). The redox-sensitive analytes clearly show that reducing conditions develop along the flowpath from Wells 16-02657 to 16-02659. Iron concentrations tend to increase at Well 16-02658, and nitrate and sulphate tend to decrease (Figure 3.4-13 through 3.4-15). All three of these changes indicate more reducing conditions at Well 16-02658. Chloride concentrations, which are not redox-sensitive, do not show any systematic changes between Wells 16-02657 and 16-02658, indicating that the changes in iron, nitrate, and sulphate are the result of changes in redox conditions rather than other processes. Wells farther down the canyon (i.e., 16-02659) also show indications of reducing conditions, but these are not as dramatic as the difference between Wells 16-02657 and 16-02658. The reason that the presence of reducing conditions is important is because nitrate and HE degradation occur under reducing conditions.



### **Figure 3.4-10. Meteoric water plot of** δ**18O and** δ**D data from shallow wells in Cañon de Valle and on the TA-16 Mesa**

Substantial amounts of barium nitrate were used at TA-16. Although nitrate concentrations are elevated, nitrate concentrations are not as high as they would be if there were no degradation. Analyses of nitrogen stable isotopes also support the conclusion of active nitrate degradation in the canyon. For the principal HE compounds (HMX, RDX, and TNT), there is also evidence of degradation products in the water at TA-16. Microbially driven degradation of HMX and RDX is favored under reducing conditions, although the concentrations of degradation products are small, suggesting only minor breakdown. The degradation of HMX and RDX can also occur from inorganic pH-controlled hydrolysis or photolysis. In contrast, robust degradation of TNT is occurring. TNT-breakdown products (e.g., amino-dinitrotoluene compounds) typically have concentrations equal to and sometimes greater than the parent TNT concentrations. TNT is more susceptible to degradation that can occur under either oxidizing or reducing conditions. The speciation and mobility of silver may also be affected by changes in redox in Cañon de Valle, although this has not been investigated in detail.

### **3.4.2.2.5 Cañon de Valle RDX and Barium Alluvial Groundwater Trends with Time**

Time-series plots of RDX and barium concentration data from alluvial groundwater samples collected in Cañon de Valle over the period from 1998 to 2002 are shown in Figures 3.4-16 and 3.4-17, respectively. Several key points are apparent from these plots:



### **Figure 3.4-11. Meteoric water plot of** δ**18O and** δ**D data from shallow wells in Martin Spring Canyon and Cañon de Valle**

- 1. RDX trends are generally stable to slightly decreasing, with occasional spikes of high concentration. The highest concentrations of RDX are measured in samples from Well 16-02657. This well is located closest to the 260 outfall. No evidence is yet apparent for the influence of the IM source removal action.
- 2. RDX concentrations in samples from Well 16-02659 (located the greatest distance east from the 260 outfall) are consistently higher than Wells 16-02655, 16-02656, and 16-02658, implying there is not a downstream trend of decreasing RDX concentration.
- 3. Barium concentration trends over time are stable to slightly decreasing, with spikes associated with pulses of barium into the system. No evidence is yet apparent for the influence of the IM source removal action.
- 4. The lowest concentration of barium is observed in the most easterly, upstream Well 16-02655, followed by Well 16-02656, and Well 16-02659. The highest barium concentration was observed in Well 16-02658. This could indicate a mass of barium mid-canyon, near Well 16-02658.

A possible model for the fluctuating pattern observed for both RDX and barium time-series concentration data involves redissolution and mobilization of contaminants in the vadose zone and alluvial system as a result of precipitation events. One manifestation of precipitation is an increase in the saturated thickness



## **Figure 3-4-12. Tritium concentrations in Cañon de Valle alluvial groundwater wells**

of alluvial groundwater in the Cañon de Valle alluvium. Figure 3.4-18 and 3.4-19 show RDX and barium concentrations in Well 16-02659 as a function of saturated thickness between 1998 and 2002. Similar plots for Wells 16-02656, 16-02657, and 16-02658 are included in Appendix H. For barium, there does not appear to be a correlation between the saturated thickness and barium concentration, whereas for RDX, a positive correlation is evident.

### **3.4.2.2.6 Additional Investigations into Cañon de Valle Seasonal Contaminant Trends**

To further investigate the potential relationships between seasonal precipitation and contaminant trends, barium, RDX, chloride, nitrate-nitrite, iron, and calcium concentrations for surface, alluvial groundwater, and spring water were plotted as a function of distance from the 260 outfall for six different seasonal flow events. These events were characterized either as high flow, moderate flow, or low flow. Data for other chemicals are presented in Appendix H.

The six events consisted of two high flow events (March 27, 2001 and May 1, 2001), two moderate flow events (July 8, 1999 and November 8, 2000), and two low flow events (September 18, 1998 and October 3, 2001). These events were also chosen on the basis of data completeness for all the alluvial groundwater, surface water, and spring data sets. Plots developed from the data included mass flow rate



**Figure 3.4-13. Variations in iron concentrations in Cañon de Valle alluvial wells and Burning Ground Spring** 

of contaminants in surface water as a function of distance downgradient (downstream or eastward) from the 260 outfall, and plots showing alluvial groundwater, spring, and surface water contaminant concentrations as a function of downstream distance from the 260 outfall.

Figures 3.4-20 and 3.4-21 show RDX and barium mass flow rate (concentration times stream volumetric flow rate) as a function of downstream distance from the 260 outfall for the high and low to moderate flow events. The highest mass flow rate of barium occurred during the March and May 2001 snowmelt runoff events. Both the low and moderate flow events showed lower mass flow rates of barium. The RDX data show relatively higher RDX concentrations during March 2001, which is likely due to extensive saturated zone input resulting from snowmelt.

Figures 3.4-22 and 3.4-23 respectively show RDX and barium concentrations in springs, alluvial groundwater, and surface water during a high flow event in March 2001. Figures 3.4-24 and 3.4-25 respectively present RDX and barium concentrations for a low flow, post-monsoon event in September 1998. Stream volumetric flow rates with distance are also plotted on these graphs. The following observations can be drawn from these graphs:



**Figure 3.4-14. Variations in nitrate concentrations in Cañon de Valle alluvial wells and Burning Ground Spring** 



**Figure 3.4-15. Variations in sulfate concentrations in Cañon de Valle alluvial wells and Burning Ground Spring** 



**Figure 3.4-16. RDX concentrations for unfiltered alluvial groundwater between 1998 and 2002 in Cañon de Valle** 



**Figure 3.4-17. Barium concentrations for unfiltered alluvial groundwater between 1998 and 2002 in Cañon de Valle** 



**Figure 3.4-18. RDX concentration in unfiltered alluvial groundwater from Well 16-02659 as a function of saturated thickness between 1998 and 2002** 



**Figure 3.4-19. Barium concentration in unfiltered alluvial groundwater from Well 16-02659 as a function of saturated thickness between 1998 and 2002** 



**Figure 3.4-20. RDX mass flow rate as a function of distance from the 260 outfall in Cañon de Valle** 



**Figure 3.4-21. Barium mass flow rate as a function of distance from the 260 outfall in Cañon de Valle** 



**Figure 3.4-22. RDX concentrations as a function of distance from the 260 outfall for March 27, 2001 snowmelt event in Cañon de Valle** 



**Figure 3.4-23. Barium concentrations as a function of distance from the 260 outfall for March 27, 2001 snowmelt event in Cañon de Valle** 



**Figure 3.4-24. RDX concentrations as a function of distance from the 260 outfall for September 18, 1998 post-monsoon precipitation event in Cañon de Valle** 



**Figure 3.4-25. Barium concentrations as a function of distance from the 260 outfall for September 18, 1998 post-monsoon precipitation event in Cañon de Valle** 

- 1. Barium concentrations are consistently highest in the alluvial groundwater and are relatively insensitive to high versus low flow conditions.
- 2. Water input from Burning Ground Spring (located approximately 500 ft from the 260 outfall) appears to dilute barium concentrations in the surface water.
- 3. RDX concentrations in groundwater were higher (with values up to 759 µg/L) during the high flow event.
- 4. RDX concentrations in the surface water were higher (with values up to 150 µg/L) during the high flow event, and, unlike low flow event data, did not show decreasing concentrations downstream.
- 5. During low flow periods, RDX concentrations were low, with the highest concentrations occurring near the 260 outfall. Downstream from Burning Ground Spring, the concentration of RDX decreased to less than 25 µg/L.

# **3.4.2.3 Martin Spring Canyon Surface Water**

A summary of all samples submitted for laboratory analyses is provided in Appendix G-1. All analytical results from Martin Spring Canyon are provided in Appendix G-3. Sample locations are shown on Figure 3.3-2.

## **3.4.2.3.1 Martin Spring Canyon Surface Water: Evaluation of Inorganic Chemicals**

A summary of all detected inorganic chemicals is provided in Table G-2.7 (located in Appendix G-2). This section includes the frequency of detected inorganic chemicals (Table 3.4-19); the screening results for inorganic chemicals that exceed the NMWQCC regulations numeric standard, or other appropriate standard (Table 3.4-20); and the inorganic chemicals retained and eliminated as COPCs (Table 3.4-21). A geochemical evaluation of naturally-occurring concentrations versus anthropogenic contribution was not performed due to the limited number of samples. The most significant inorganic chemical COPCs for Martin Spring Canyon surface water are barium, boron, and manganese. A brief description of the retained inorganic COPCs with concentrations exceeding standards is provided in Appendix I-4.

## **3.4.2.3.2 Martin Spring Canyon Surface Water: Evaluation of Organic Chemicals**

A summary of all detected organic chemicals is provided in Table G-2.8 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-22), the screening results for organic chemicals with concentrations exceeding the NMWQCC regulations numeric standard, or other appropriate standard (Table 3.4-23), and the organic chemicals retained and eliminated as COPCs (Table 3.4-24). Only RDX was retained as a COPC.

## **3.4.2.4 Martin Spring Canyon Alluvial Groundwater**

This section presents the results from the quarterly groundwater sampling of alluvial wells in Martin Spring Canyon. A summary of all samples submitted for laboratory analyses is provided in Appendix G-1. All analytical data from Martin Spring Canyon are provided in Appendix G-3. Sample locations are shown on Figure 3.3-2.









*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table. b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

c<br>n/a = Not applicable.

### **3.4.2.4.1 Martin Spring Canyon Alluvial Groundwater: Evaluation of Inorganic Chemicals**

A summary of detected inorganic chemicals is provided in Table G-2.9 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-25), the screening results for inorganic chemicals that exceed the NMWQCC regulations numeric standard, or other appropriate standard (Table 3.4-26), and the inorganic chemicals retained and eliminated as COPCs (Table 3.4-27).





**Table 3.4-20 (continued)** 

Chemical	Sample ID	Concentration Sample (Hârl)			NMWQCC Standard (Hârl)	EPA MCL (µg/L)	Tap Water PRG EPA Region 6 (Hôrl)	Screening Limit Exceeds
Nitrate	RE16-99-3060	Max. Detected Value	3300		10000 <sup>9</sup>	10000	n/a	<b>No</b>
	RE16-99-3062	Max. Undetected Value	200	(U)	10000 <sup>9</sup>	10000	n/a	No
Nitrate-Nitrite	RE16-98-3101	Max. Detected Value	5600		10000 <sup>9</sup>	na	n/a	No
as N	RE16-00-3309	Max. Undetected Value	500	(U)	10000 <sup>9</sup>	na	n/a	No
Potassium	RE16-99-3062	Max. Detected Value	9500		na	na	na	na
Selenium	RE16-99-3062	Max. Detected Value	38.3		$5^{\circ}$	50	n/a	Yes
	RE16-00-3181	Max. Undetected Value	4.5	(U)	$5^j$	50	n/a	No
Silver	RE16-99-3062	Max. Detected Value	5.5	(J)	50 <sup>9</sup>	100	n/a	No
	RE16-98-3103	Max. Undetected Value	5	(U)	50 <sup>9</sup>	100	n/a	<b>No</b>
Sodium	RE16-00-3309	Max. Detected Value	43500		na	na	na	na
Sulfate	RE16-00-3309	Max. Detected Value	70300		600000	250000	n/a	No
Thallium	RE16-00-3264	Max. Detected Value	0.0819	(J)	n/a	$\overline{2}$	n/a	<b>No</b>
	RE16-99-3062	Max. Undetected Value	45	(U)	n/a	$\overline{2}$	n/a	Yes
Uranium	RE16-00-3180	Max. Detected Value	8.15		5000 <sup>9</sup>	30	n/a	No
Vanadium	RE16-99-3062	Max. Detected Value	111		100 <sup>c</sup>	na	n/a	Yes
	RE16-00-3264	Max. Undetected Value	3.91	(U)	$100^{\circ}$	na	n/a	No
Zinc	RE16-99-3062	Max. Detected Value	183		10000	5000	n/a	No
	RE16-00-3311	Max. Undetected Value	31.7	(U)	10000	5000	n/a	No

*Sources:* 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; and EPA 2003, 76867.

 $a(J+)$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.

b NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3.3103).

c NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $d$  n/a = Not applicable.

 $e$  (U) = The chemical is classified "undetected."

 $f(t)$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

g NMWQCC Groundwater Human Health Standards (20 NMAC 6.2.3103).

 $h$  na = Not available.

<sup>i</sup> NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

j NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900).

The majority of inorganic chemical COPCs were detected in Well 16-06295. COPCs include arsenic, barium, beryllium, boron, cadmium, lead, and manganese. A brief description of the retained inorganic COPCs with concentrations exceeding standards is provided in Appendix I-4.





### **3.4.2.4.2 Martin Spring Canyon Alluvial Groundwater: Evaluation of Organic Chemicals**

A summary of the detected organic chemicals is provided in Table G-2.10 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-28), the screening results for organic chemicals that exceed the NMWQCC regulations numeric standards, or other appropriate standards (Table 3.4-29), and the organic chemicals retained and eliminated as COPCs (Table 3.4-30). Only RDX was retained as a COPC.

<b>Chemical</b>	<b>Field</b> Preparation	Number of <b>Analyses</b>	Number of <b>Detects</b>	<b>Concentration Range</b> $(\mu g/L)$	<b>Percent Detected</b> for 20 Samples or Greater <sup>a</sup>	
Amino-2,6-dinitrotoluene[4-]	Filtered	$\overline{2}$	1	$[0.2]^{b}$ to 2.2	$n/a^c$	
	Unfiltered	11	$\overline{2}$	$[0.2]$ to $[5]$		
Amino-4,6-dinitrotoluene[2-]	Filtered	2	1	$[0.2]$ to 1.9	n/a	
	Unfiltered	11	$\overline{2}$	$[0.2]$ to $[5]$		
Amino-x,6-dinitrotoluene[x-]	Unfiltered	1	1	$2.3$ to $2.3$	n/a	
Dinitrobenzene[1,3-]	Filtered	$\overline{2}$	1	$[0.2]$ to 0.66	n/a	
<b>HMX</b>	Filtered	2	$\overline{2}$	7.8 to 20	n/a	
	Unfiltered	$12 \overline{ }$	8	$[1]$ to 25		
<b>RDX</b>	Filtered	2	$\overline{2}$	60 to 160	n/a	
	Unfiltered	$12 \overline{ }$	10	$[0.84]$ to 200		
Trinitrobenzene[1,3,5-]	Filtered	2	1	$[0.2]$ to 1	n/a	
	Unfiltered	12	1	$[0.1]$ to $[5]$		

**Table 3.4-22 Frequency of Detected Organic Chemicals in Martin Spring Canyon Surface Water Samples** 

*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br>b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$ <sub>n/a</sub> = Not applicable.

## **3.4.2.4.3 Martin Spring Canyon Alluvial Groundwater: Evaluation of Tritium**

The summary of detected tritium in samples collected in Martin Spring Canyon alluvial groundwater is shown in Table G-2.11 (located in Appendix G-2). Tritium was the radionuclide detected in Martin Spring Canyon surface water. The frequency of detection of tritium (Table 3.4-31), the screening results (Table 3.4-32), and the retained/eliminated analysis (Table 3.4-33) are presented in this section. The results show that tritium was not present above either the EPA MCL or the NMWQCC standard.

## **3.4.2.4.4 Martin Spring Canyon Alluvial Groundwater: Well Level and Water Chemistry**

Without consistent rainfall or snowmelt input, the uppermost alluvial well (Well 16-06293) in Martin Spring Canyon is typically dry. Martin Spring alone provides sustained discharge to maintain a saturated zone in the alluvium where the well is located. The middle and lowermost wells (Wells 16-06294 and 16-06295) show fluctuating saturated thickness in response to both sustained rainfall and snowmelt inputs. Complete quarterly tabular data records with depth to water, temperature, conductivity, and pH measurements are included in Appendix H.

## **3.4.2.5 Cañon de Valle and Martin Spring Sediment**

Solid media sampling included alluvial sediment sampling in both Cañon de Valle and Martin Spring Canyon as well as sampling of alluvium and tuff in Martin Spring Canyon boreholes. In Martin Spring


<b>Chemical</b>	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Amino-2,6-dinitrotoluene[4-]	Eliminated	No values above screening limit.
Amino-4,6-dinitrotoluene[2-]	Eliminated	No values above screening limit.
Amino-x,6-dinitrotoluene[x-]	Eliminated	No values above screening limit.
Dinitrobenzene[1,3-]	Eliminated	No values above screening limit.
<b>HMX</b>	Eliminated	No values above screening limit.
<b>RDX</b>	<b>Retained</b>	Maximum value exceeded screening limit.
Trinitrobenzene[1,3,5-]	Eliminated	No values above screening limit.

**Table 3.4-24 Retained and Eliminated Organic Chemicals in Martin Spring Canyon Surface Water Samples** 

Canyon, three boreholes were drilled and subsequently completed as monitoring wells during the Phase III RFI (see Figure 3.3-2). The boreholes were sampled at discrete intervals that represent alluvium (Qal) and Bandelier tuff (Qbt 4). A summary of the laboratory analyses requested for all solid media samples is provided in Appendix G-1. All analytical data are presented in Appendix G-3. Figure 3.3-9 shows the location of the sediment samples.

Results from geomorphic sampling conducted in the Cañon de Valle and Martin Spring Canyon during 1999 and 2000 are also summarized in this section. Geomorphic sampling results provide important information on the distribution of contaminants across the various sediment types, and are important in the development of the conceptual site model. Ultimately, knowledge of contaminant inventory distribution will help focus the CMS.

# **3.4.2.5.1 Cañon de Valle Sediment: Evaluation of Inorganic Chemicals**

A summary of all detected inorganic chemicals is provided in Table G-2.12 (located in Appendix G-2). This section includes the frequency of detected inorganic chemicals and the screening to BVs and statistical background comparisons (see Appendix I-1 and Table 3.4-34). Table 3.4-35 presents the list of detected inorganic chemicals retained and eliminated as COPCs. The results of the screening process indicate significant inorganic chemical COPCs in the Cañon de Valle sediment include antimony, barium, cobalt, copper, lead, nickel, and silver. A brief description of the retained COPCs with concentrations exceeding limits is provided in Appendix I-4.

# **3.4.2.5.2 Cañon de Valle Sediment: Evaluation of Organic Chemicals**

A summary of all detected organic chemicals is provided in Table G-2.13 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-36). Table 3.4-37 presents the list of detected organic chemicals retained and eliminated as COPCs. The results of the screening process indicate that amino-2,6-dinitrotoluene[4-], amino-4,6-dinitrotoluene[2-], HMX, RDX, and TNT are the most significant retained organic COPCs. A brief description of the retained organic COPCs with concentrations exceeding the screening limits is provided in Appendix I-4.

# **3.4.2.5.3 Martin Spring Canyon Alluvium, Sediment and Tuff: Evaluation of Inorganic Chemicals**

A summary of all detected inorganic chemicals is summarized in Table G-2.14 (located in Appendix G-2). This section includes the frequency of detected inorganic chemicals and the screening to BVs and

Chemical	<b>Field</b> Preparation	Number of <b>Analyses</b>	Number of <b>Detects</b>	<b>Concentration Range</b> $(\mu g/L)$	<b>Percent Detected for 20</b> Samples or Greater <sup>a</sup>	
Aluminum	Filtered	13	13	300 to 9300	100	
	Unfiltered	17	17	1420 to 530000		
Antimony	Filtered	12	$\overline{\mathbf{4}}$	0.803 to 3.6	32	
	Unfiltered	16	5	1.08 to 3.4		
Arsenic	Filtered	13	7	$[0.69]^{b}$ to 6.2	73	
	Unfiltered	17	15	[0.69] to 132		
<b>Barium</b>	Filtered	13	13	85.9 to 300	100	
	Unfiltered	17	17	148 to 38000		
Beryllium	Filtered	13	$6\phantom{1}$	0.09 to 0.22	63	
	Unfiltered	17	13	[0.16] to 78		
Boron	Filtered	13	12	170 to 2250	93	
	Unfiltered	17	16	175 to 2180		
Cadmium	Filtered	13	$\mathbf{3}$	0.0816 to 1.4	37	
	Unfiltered	17	8	[0.24] to 70		
Calcium	Filtered	13	13	6070 to 27000	100	
	Unfiltered	17	17	7400 to 130000		
Chloride	Unfiltered	15	15	5830 to 43100	$n/a^c$	
Chromium	Filtered	13	11	$[0.64]$ to 4.4	83	
	Unfiltered	17	14	[0.64] to 1200		
Cobalt	Filtered	13	6	$[0.9]$ to $9.05$	60	
	Unfiltered	17	12	$[0.88]$ to $[380]$		
Copper	Filtered	13	11	[2.4] to 15.7	80	
	Unfiltered	17	13	$[2.6]$ to 860		
Fluoride	Unfiltered	15	15	107 to 571	n/a	
Iron	Filtered	13	13	254 to 4790	100	
	Unfiltered	17	17	761 to 1100000		
Lead	Filtered	13	$\boldsymbol{9}$	[0.77] to 3.72	83	
	Unfiltered	17	16	$[1.2]$ to 995		
Magnesium	Filtered	13	13	1660 to 6440	100	
	Unfiltered	17	17	2520 to 80000		
Manganese	Filtered	13	13	3.4 to 3340	100	
	Unfiltered	17	17	33.3 to 37000		
Mercury	Filtered	13	$\ensuremath{\mathsf{3}}$	[0.04] to [0.34]	40	
	17 Unfiltered		9	0.057 to 4.1		
Nickel	Filtered	13	10	$[1.1]$ to $[40]$	77	
	Unfiltered	17	13	$[1.2]$ to 450		

**Table 3.4-25 Frequency of Detected Inorganic Chemicals in Martin Spring Canyon Alluvial Groundwater Samples** 

<b>Chemical</b>	<b>Field</b> Preparation	Number of <b>Analyses</b>	Number of <b>Detects</b>	<b>Concentration Range</b> $(\mu g/L)$	<b>Percent Detected for 20</b> Samples or Greater <sup>a</sup>
Nitrate-Nitrite as N	Unfiltered	15	8	[50] to 1600	n/a
Perchlorate	Unfiltered	15	1	[4] to 17	n/a
Potassium	Filtered	13	13	1700 to 9770	100
	Unfiltered	17	17	4440 to 82000	
Selenium	Filtered	13	1	$[0.454]$ to $[4.5]$	17
	Unfiltered	17	$\overline{4}$	[0.79] to 29.6	
Silver	Filtered	13	$\overline{2}$	0.0546 to [10]	23
	Unfiltered	17	5	0.974 to [160]	
Sodium	Filtered	13	13	8180 to 54300	100
	Unfiltered	17	17	10600 to 54700	
Sulfate	Unfiltered	15	15	10500 to 73900	n/a
Thallium	Filtered	13	3	$0.0634$ to [3.8]	23
	Unfiltered	17	$\overline{4}$	[0.044] to 6.16	
Uranium	Unfiltered	6	$6\phantom{1}$	0.181 to 20.4	n/a
Vanadium	Filtered	13	12	$[1.3]$ to 8.8	93
	Unfiltered	17	16	2.8 to 1100	
Zinc	Filtered	13	8	9.6 to 79	80
	Unfiltered	17	16	11.7 to 6600	

**Table 3.4-25 (continued)** 

*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

c<br>n/a = Not applicable.

statistical background comparisons (see Appendix I-1 and Table 3.4-38). Table 3.4-39 presents the list of detected inorganic chemicals retained and eliminated as COPCs. The results of the screening process indicate that arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, and silver are significant inorganic COPCs. The maximum concentration for most of these COPCs was detected at Location ID 16-06600, located within the southern tributary of Martin Spring Canyon. A brief description of retained inorganic COPCs with concentrations exceeding screening limits for Martin Spring Canyon alluvium, sediment, and tuff is provided in Appendix I-4.

## **3.4.2.5.4 Martin Spring Canyon Alluvium, Sediment and Tuff: Evaluation of Organic Chemicals**

A summary of all detected organic chemicals is provided in Table G-2.15 (located in Appendix G-2). This section includes the frequency of detected organic chemicals (Table 3.4-40). Table 3.4-41 presents the list of detected organic chemicals retained and eliminated as COPCs. The prevalent organic COPCs in Martin Spring Canyon sediment and tuff are amino-2,6-dinitrotoluene [4-], amino-4,6-dinitrotoluene [2-], RDX, and TNT. A brief description of the retained organic COPCs which exceed screening limits is provided in Appendix I-4.

Chemical	Sample ID	Concentration Sample (Hôn)	NMMOCC <b>Standard</b> (Hêrl)	EPA MCL (µg/L)	EPA Region 6 Tap Water PRG (Hôrl)	Screening Limit Exceeds		
Aluminum	RE16-00-3280	Max. Detected Value	530000	$(J)^a$	$5000^{b,c}$	50	na <sup>d</sup>	Yes
Antimony	RE16-01-3014	Max. Detected Value	3.6	(J)	na	6	na	No
	RE16-01-3013	Max. Undetected Value	3.2	$(U)^e$	na	6	na	No
Arsenic	RE16-00-3280	Max. Detected Value	132		$100^T$	10	na	Yes
	RE16-00-3124	Max. Undetected Value	4	(U)	$100^{\dagger}$	10	na	No
<b>Barium</b>	RE16-00-3280	Max. Detected Value	38000	(J)	1000 <sup>f</sup>	2000	na	Yes
Beryllium	RE16-00-3280	Max. Detected Value	78		na	4	na	Yes
	RE16-01-3011	Max. Undetected Value	0.22	(U)	na	$\overline{4}$	na	No
Boron	RE16-00-3302	Max. Detected Value	2250		$750^{\overline{b}}$	n/a <sup>9</sup>	na	Yes
	RE16-00-3123	Max. Undetected Value	500	(U)	750 <sup>b</sup>	n/a	na	<b>No</b>
Cadmium	RE16-00-3280	Max. Detected Value	70	$(J+)^h$	$10^{\text{f}}$	5	na	Yes
	RE16-01-3011	Max. Undetected Value	0.92	(U)	$10^{\text{f}}$	5	na	No
Calcium	RE16-00-3280	Max. Detected Value	130000	(J)	n/a	n/a	n/a	n/a
Chloride	RE16-01-3045	Max. Detected Value	43100		250000	250000	na	No
Chromium	RE16-00-3280	Max. Detected Value	1200		$50^{\circ}$	100	na	Yes
	RE16-01-3174	Max. Undetected Value	4	(U)	$50^{\dagger}$	100	na	No
Cobalt	RE16-00-3199	Max. Detected Value	125		50 <sup>b</sup>	n/a	na	Yes
	RE16-00-3280	Max. Undetected Value	380	(U)	50 <sup>b</sup>	n/a	na	Yes
Copper	RE16-00-3280	Max. Detected Value	860		$500^{\rm c}$	1000	na	Yes
	RE16-00-3226	Max. Undetected Value	56.9	(U)	$500^{\circ}$	1000	na	No
Fluoride	RE16-00-3199	Max. Detected Value	571		1600 <sup>t</sup>	2000	na	No
Iron	RE16-00-3280	Max. Detected Value	1100000	$(J-)$	1000	300	na	Yes
Lead	RE16-00-3280	Max. Detected Value	995		$50^{\text{f}}$	15	na	Yes
	RE16-00-3245	Max. Undetected Value	3.53	(U)	$50^{\dagger}$	15	na	No
Magnesium	RE16-00-3280	Max. Detected Value	80000 (J)		n/a	n/a	n/a	n/a
Manganese	RE16-00-3280	Max. Detected Value	37000	(J)	200'	50	na	Yes
Mercury	RE16-00-3280	Max. Detected Value	4.1		$0.77^k$	$\overline{2}$	na	Yes
	RE16-01-3014	Max. Undetected Value	0.34	(U)	$0.77^k$	$\overline{2}$	na	No
Nickel	RE16-00-3280	Max. Detected Value	450		200 <sup>b</sup>	n/a	na	Yes
	RE16-00-3124	Max. Undetected Value	40	(U)	200 <sup>b</sup>	n/a	na	No.
Nitrate-Nitrite	RE16-00-3226	Max. Detected Value	1600		10000 <sup>†</sup>	n/a	na	No
as N	RE16-01-3013	Max. Undetected Value	1000 (U)		10000 <sup>f</sup>	n/a	na	No

**Table 3.4-26 Screening of Inorganic Chemicals Detected in Martin Spring Canyon Alluvial Groundwater Samples** 

**Table 3.4-26 (continued)** 

Chemical	Sample ID	Concentration Sample (Hârl)	NMMOCC <b>Standard</b> (Thôn)	EPA MCL (µg/L)	Tap Water PRG $\bullet$ EPA Region (Tiêrl)	Screening Limit Exceeds		
Perchlorate	RE16-00-3123	Max. Detected Value	17		$4^{\mathsf{I}}$	n/a	na	Yes
	RE16-00-3280	Max. Undetected Value	4.16	(U)	4 <sup>1</sup>	n/a	na	Yes
Potassium	RE16-00-3280	Max. Detected Value	82000	(J)	n/a	n/a	n/a	n/a
Selenium	RE16-00-3280	Max. Detected Value	29.6	$(J+)$	$5^k$	50	na	Yes
	RE16-00-3123	Max. Undetected Value	8	(UJ)	$5^k$	50	na	Yes
Silver	RE16-01-3174	Max. Detected Value	28		$50^{\dagger}$	100	na	No.
	RE16-00-3280	Max. Undetected Value	160	(U)	$50^{\dagger}$	100	na	Yes
Sodium	RE16-01-3045	Max. Detected Value	54700		n/a	n/a	n/a	n/a
Sulfate	RE16-00-3301	Max. Detected Value	73900		600000	250000	na	No
Thallium	RE16-00-3280	Max. Detected Value	6.16		na	2	na	Yes
	RE16-00-3199	Max. Undetected Value	3.8	(U)	na	$\overline{2}$	na	Yes
Uranium	RE16-00-3199	Max. Detected Value	20.4		$5000^T$	30	na	No
Vanadium	RE16-00-3280	Max. Detected Value	1100		$100^{\circ}$	n/a	na	Yes
	RE16-01-3174	Max. Undetected Value	8.4	(U)	100 <sup>c</sup>	n/a	na	No.
Zinc	RE16-00-3280	Max. Detected Value	6600		10000'	5000	na	Yes
	RE16-00-3303	Max. Undetected Value	43.9	(U)	10000	5000	na	No

*Sources:* 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; (EPA 2003, 76867; California DHS 2003, 76862.

 $a$ (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

<sup>b</sup> NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3.3103).

<sup>c</sup> NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $d$  n/a = Not applicable.

 $e(U)$  = The chemical is classified "undetected."

f NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

 $9$  na = Not available.

 $h(J+)$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.

<sup>i</sup> NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

 $j$  (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias.

k NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900).

<sup>I</sup> California DHS 2003, 76862.

m (UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain than usual.





Chemical	<b>Field</b> Preparation	Number of <b>Analyses</b>	Number of <b>Detects</b>	<b>Concentration</b> Range (µg/L)	<b>Percent Detected for 20</b> Samples or Greater <sup>a</sup>
Amino-x,6-dinitrotoluene[x-]	Unfiltered	3		$[0.39]$ <sup>b</sup> to 0.66	$n/a^c$
Carbon Disulfide	Unfiltered	9	2	$[1]$ to $[5]$	n/a
<b>HMX</b>	Unfiltered	12	3	$[0.1]$ to $[13]$	n/a
<b>RDX</b>	Unfiltered	13	5	[0.1] to 23	n/a
Trinitrobenzene[1,3,5-]	Unfiltered	12		$[0.1]$ to $[1]$	n/a
Trinitrotoluene[2,4,6-]	Unfiltered	12		$[0.1]$ to $[1]$	n/a

**Table 3.4-28 Frequency of Detected Organic Chemicals in Martin Spring Canyon Alluvial Groundwater Samples** 

*Source:* EPA 1989, 08021.<br> **The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less<br>
than expected due to the inclusion of undetects not reported** 

than expected due to the inclusion of undetects not reported by this table.<br><sup>b</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$ <sub>n/a</sub> = Not applicable.

#### **3.4.2.5.5 Sediment Contamination and Geomorphology**

An investigation of COPCs contained within sediment deposits in Cañon de Valle and Martin Spring Canyon was conducted in 1999 and 2000 (see section 3.3.4.2). This investigation focused on characterizing the concentrations, distribution, and inventory of barium and the HE chemicals HMX and RDX in fine-grained sediment deposits. The full report is included in Appendix E.

The most intensive geomorphic characterization was conducted downstream from the 260 outfall, in reaches CDV-2 West and CDV-2 East (see Figure 3.4-26), because higher levels of contaminants were expected there relative to the other reaches. No characterization was conducted in reach CDV-2 Central, which was an exclusion area for MDA P remediation activities at the time of this investigation, although this area was mapped. Characterization was less intensive in Martin Spring Canyon, where the presence of contamination in sediment was unknown.

Basic geomorphic unit designations used in previous studies in other canyons were also adopted in this investigation. The area of potential contamination associated with flooding in Cañon de Valle and Martin Spring Canyon was divided into areas occupied by the stream channel since 1942 (labeled "c"), and adjoining floodplain areas that experienced overbank flooding (labeled "f"). Floodplain areas typically include pre-1942 trees, whereas only younger trees, shrubs, or grass are present on the abandoned channel surfaces. Channel areas were further subdivided into the active channel (c1) and abandoned channels that contain deposits of fine-grained sediment overlying coarse channel deposits (c2 and c3,



 $\frac{a}{b}(J)$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.<br><sup>b</sup> na = not available.

na = not available.

(U) = The chemical is classified "not detected."

o o  $(UJ)$  = The chemical is classified "not detected" with an expectation that the reported result is more uncertain than usual.

## **Table 3.4-30 Retained and Eliminated Organic Chemicals in Martin Spring Canyon Alluvial Groundwater Samples**



**Table 3.4-31** 

## **Frequency of Detected Tritium in Martin Spring Canyon Alluvial Groundwater Samples**



(\*)*Source:* EPA 1989, 08021.

## **Table 3.4-32 Screening of Tritium Detected in Martin Spring Canyon Alluvial Groundwater Samples**



*Sources:* 20 NMAC 6.2.3103, "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900, "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $b$  n/a = Not applicable.

## **Table 3.4-33**

#### **Retained and Eliminated Tritium in Martin Spring Canyon Alluvial Groundwater Samples**







*Sources*: LANL 1998, 59730 and EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of

than expected due to the inclusion of understanding by the inclusion of the inclusion of values in brackets are below detection limits, although some chemicals may be detected at values within this range.

c<br><sup>c</sup> na = Not available.

where c2 units are lower in elevation relative to the channel and inferred to be younger than c3). Floodplain areas were subdivided into areas that had strong evidence for post-1942 flooding (f1) and areas that might have been flooded but where the evidence was less conclusive (f2). Adjacent areas were locally mapped, using the standard geologic designation "Q" for Quaternary units (Qal = alluvium;  $Qbt$  = Bandelier Tuff,  $Qc$  = colluvium,  $Qf$  = fan, and  $Qt$  = stream terrace). Note that some of these areas could contain contaminants derived from mesa top SWMUs (e.g., Qf below MDA R). A preliminary





\*See Appendix I-1 for further discussion.

Chemical	Number of <b>Analyses</b>	Number of <b>Detects</b>	<b>Concentration Range</b> (mg/kg)	<b>Percent Detected for 20</b> Samples or Greater <sup>a</sup>
Amino-2,6-dinitrotoluene[4-]	46	22	$[0.08]^{b}$ to [5]	48
Amino-4,6-dinitrotoluene[2-]	46	22	0.0393 to [5]	48
Benzo(a)pyrene	16	1	$[0.0339]$ to $[0.93]$	$n/a^c$
Benzoic Acid	16	3	$0.23$ to $[2.3]$	n/a
Di-n-butylphthalate	16	1	[0.058] to [0.93]	n/a
Fluoranthene	16	2	0.0177 to [0.91]	n/a
Hexachlorobenzene	16	1	0.0756 to [0.93]	n/a
<b>HMX</b>	46	33	[0.08] to 290	72
Indeno(1,2,3-cd)pyrene	16	1	[0.0339] to [0.93]	n/a
Methylphenol[4-]	16	$\overline{2}$	0.141 to [0.93]	n/a
Naphthalene	16	1	[0.0339] to [0.93]	n/a
Nitrobenzene	53	1	$[0.08]$ to $[5.2]$	$\overline{2}$
Pyrene	16	3	0.0187 to [0.91]	n/a
Pyridine	16	1	0.16 to [0.93]	n/a
<b>RDX</b>	46	27	0.0615 to [20]	59
Trinitrobenzene[1,3,5-]	46	1	$[0.08]$ to $[5]$	2
Trinitrotoluene[2,4,6-]	46	20	$[0.08]$ to $[5]$	43

**Table 3.4-36 Frequency of Detected Organic Chemicals in Cañon de Valle Alluvial Sediment Samples** 

*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b<br>Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$ <sub>n/a</sub> = Not applicable.

geomorphic map was made based on topography and vegetation, and the map was iteratively revised as more detailed characterization data became available.

#### Screening Data

Screening data indicated low levels of silver (average concentration of less than 100 mg/kg by XRF) in all geomorphic units in all reaches except CDV-1 West, immediately downstream from the TA-16 silver outfall. In this reach, the two samples from c1 had the highest concentrations (957 and 2595 mg/kg), and f1 had concentrations as high as 364 mg/kg.

Screening data indicate low levels of barium (average concentration of less than 600 mg/kg by XRF) in all geomorphic units and all reaches upstream from MDA R, and higher levels in all downstream reaches. The data indicate both the MDA R area and the 260 outfall contributed substantial amounts of barium to Cañon de Valle sediment, with concentrations increasing downstream from each of these sources. Concentrations are lower downstream of MDA P, indicating it is not a major source.

**Table 3.4-37 Retained and Eliminated Organic Chemicals in Cañon de Valle Alluvial Sediment Samples** 

<b>Chemical</b>	Retained/ <b>Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Amino-2,6-dinitrotoluene[4-]	<b>Retained</b>	22 samples are above the detection limit.
Amino-4,6-dinitrotoluene[2-]	<b>Retained</b>	22 samples are above the detection limit.
Benzo(a)pyrene	<b>Retained</b>	1 sample is above the detection limit.
Benzoic Acid	<b>Retained</b>	3 samples are above the detection limit.
Di-n-butylphthalate	<b>Retained</b>	1 sample is above the detection limit.
Fluoranthene	<b>Retained</b>	2 samples are above the detection limit.
Hexachlorobenzene	<b>Retained</b>	1 sample is above the detection limit.
<b>HMX</b>	<b>Retained</b>	33 samples are above the detection limit.
Indeno(1,2,3-cd)pyrene	<b>Retained</b>	1 sample is above the detection limit.
Methylphenol[4-]	<b>Retained</b>	2 samples are above the detection limit.
Naphthalene	<b>Retained</b>	1 sample is above the detection limit.
Nitrobenzene	Eliminated	Greater than 20 analyses were taken and the number of detects comprise less than 5% of the total number of analyses.
Pyrene	<b>Retained</b>	3 samples are above the detection limit.
Pyridine	<b>Retained</b>	1 sample is above the detection limit.
<b>RDX</b>	<b>Retained</b>	27 samples are above the detection limit.
Trinitrobenzene[1,3,5-]	Eliminated	Greater than 20 analyses were taken and the number of detects comprise less than 5% of the total number of analyses.
Trinitrotoluene[2,4,6-]	<b>Retained</b>	20 samples are above the detection limit.

Screening data for RDX are all below detection limits for reaches CDV-1 West, CDV-1 Central, and CDV-1 East, and are above detection limits in over 50% of the samples in downstream reaches. The values obtained in CDV-2 West and CDV-2 East samples were similar to CDV-1 values.

The highest levels of barium as analyzed by XRF were found in the c3 and f1 units in reach CDV-2 West, downstream from the 260 outfall. These include all concentrations greater than 13,000 mg/kg in Cañon de Valle, with some concentrations as high as 48,000 mg/kg. In comparison, the maximum concentration in the c2 unit of CDV-2 West, lower in elevation and generally closer to the channel, was 6400 mg/kg. In reach CDV-2 East, the highest concentrations of barium were also found in the c3 and f1 units, although the relative difference between these units and c2 was much less than in CDV-2 West. In contrast, levels of barium by XRF are similar in the c2 and c3 units of CDV-1 East, and lower in f1. Limited XRF analyses from coarse-grained samples indicate the presence of barium in all reaches downstream from MDA R at levels higher than in upstream reaches, but lower than in fine-grained samples from these reaches.

#### Off-Site Laboratory Results

General trends in laboratory-analyzed barium concentration in fine-grained sediment deposits are consistent with data from the screening samples: concentrations are highest in reach CDV-2 West, downstream from the 260 outfall, but also are present above background upstream from the

Chemical	Media Code	Number of Analyses	Number of <b>Detects</b>	Concentration Range (mg/kg)	BV (mg/kg)	Number of Above BV <b>Detects</b>	Number of Non- Detects Above $\mathbf{S}$	<b>Percent Detected</b> for 20 Samples or Greater <sup>a</sup>
Aluminum	Qal	3	3	5000 to 16000	15400 <sup>b</sup>	$\mathbf 1$	0	n/a <sup>c</sup>
	Qbt 4	3	3	1700 to 2900	7340	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	8500 to 17000	15400	$\mathbf{1}$	$\pmb{0}$	100
Antimony	Qal	3	$\overline{2}$	0.1 to $[0.53]$ <sup>d</sup>	0.83	$\pmb{0}$	0	n/a
	Qbt 4	3	0	$[0.52 \text{ to } 0.56]$	0.5	$\pmb{0}$	$\ensuremath{\mathsf{3}}$	n/a
Arsenic	Qal	$\ensuremath{\mathsf{3}}$	3	2.1 to 4.1	3.98	$\mathbf{1}$	$\mathsf 0$	n/a
	Qbt 4	3	3	1.6 to 1.9	2.79	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	2.6 to 10	3.98	$\overline{7}$	$\mathsf 0$	100
<b>Barium</b>	Qal	3	3	53 to 180	127	$\mathbf{1}$	$\pmb{0}$	n/a
	Qbt 4	3	$\mathbf{3}$	15 to 41	46	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	86 to 1700	127	10	$\mathsf 0$	100
Beryllium	Qal	3	3	0.42 to 0.82	1.31	0	$\pmb{0}$	n/a
	Qbt 4	3	$\mathbf{3}$	0.3 to 0.85	1.21	$\pmb{0}$	$\mathsf 0$	n/a
	Sed	20	20	0.55 to 1	1.31	0	$\mathsf 0$	100
Boron	Qal	3	0	[27 to 30]	na <sup>e</sup>	na	na	n/a
	Qbt 4	3	$\pmb{0}$	[26 to 28]	na	na	na	n/a
	Sed	20	18	[0.0726] to 43	na	na	na	90
Cadmium	Qal	3	3	0.05 to 0.16	0.4	$\pmb{0}$	$\pmb{0}$	n/a
	Qbt 4	3	3	0.06 to 0.07	1.63	$\mathbf 0$	0	n/a
	Sed	20	20	0.048 to 1	0.4	$\mathbf 5$	$\mathsf{O}\xspace$	100
Calcium	Qal	3	3	560 to 1600	4420	$\pmb{0}$	$\mathbf 0$	n/a
	Qbt 4	3	$\mathsf 3$	280 to 450	2200	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	1700 to 4900	4420	$\mathbf{1}$	$\mathsf 0$	100
Chromium	Qal	$\overline{3}$	$\mathbf{3}$	5.2 to 8.1	10.5	$\mathbf 0$	$\pmb{0}$	n/a
	Qbt 4	3	$\mathbf{3}$	1.5 to $14$	7.14	$\mathbf{1}$	0	n/a
	Sed	20	20	5.2 to 30	10.5	$\overline{7}$	0	100
Cobalt	Qal	3	3 <sup>1</sup>	1.5 to $3.4$	4.73	0	0	n/a
	Qbt 4	3	3	0.78 to 1.5	3.14	0	0	n/a
	Sed	20	20	2.9 to 5.8	4.73	$\overline{2}$	0	100
Copper	Qal	$\mathbf{3}$	3	2.8 to 4.8	$11.2$	0	0	n/a
	Qbt 4	3	3	1.8 to 2.3	4.66	0	0	n/a
	Sed	20	20	4.9 to 100	11.2	$\overline{7}$	$\pmb{0}$	100

**Table 3.4-38 Frequency of Detected Inorganic Chemicals in Martin Spring Canyon Alluvium, Sediment, and Tuff Samples** 

**Table 3.4-38 (continued)** 

Chemical	Media Code	Number of Analyses	Number of <b>Detects</b>	Concentration Range (mg/kg)	(mg/kg) (mg/kg)	Number of Above BV <b>Detects</b>	Number of Non- Detects Above $\mathbf{\underline{s}}$	<b>Percent Detected</b> for 20 Samples or Greater <sup>a</sup>
Iron	Qal	3	3	8700 to 14000	13800	$\mathbf{1}$	0	n/a
	Qbt 4	3	3	7400 to 7800	14500	0	0	n/a
	Sed	20	20	7200 to 16000	13800	$\mathbf 1$	$\pmb{0}$	100
Lead	Qal	$\ensuremath{\mathsf{3}}$	3	6.3 to 18	19.7	$\pmb{0}$	$\pmb{0}$	n/a
	Qbt 4	3	3	2.1 to 5.1	11.2	$\pmb{0}$	0	n/a
	Sed	20	20	11 to 120	19.7	$\boldsymbol{9}$	0	100
Magnesium	Qal	$\ensuremath{\mathsf{3}}$	$\ensuremath{\mathsf{3}}$	540 to 1900	2370	$\pmb{0}$	$\pmb{0}$	n/a
	Qbt 4	3	3	240 to 340	1690	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	1300 to 2400	2370	1	0	100
Manganese	Qal	3	$\ensuremath{\mathsf{3}}$	150 to 220	543	$\pmb{0}$	$\mathsf 0$	n/a
	Qbt 4	3	3	270 to 330	482	$\mathbf 0$	$\mathbf 0$	n/a
	Sed	$\ensuremath{\mathsf{3}}$	3	130 to 870	543	1	0	n/a
Mercury	Qal	$\ensuremath{\mathsf{3}}$	3	0.01 to 0.02	0.1	0	0	n/a
	Qbt 4	3	$\pmb{0}$	$[0.1 \text{ to } 0.11]$	0.1	$\pmb{0}$	$\overline{c}$	n/a
	Sed	20	20	0.042 to 2.3	0.1	18	0	100
Nickel	Qal	$\ensuremath{\mathsf{3}}$	3	2.6 to 5.9	9.38	0	$\pmb{0}$	n/a
	Qbt 4	3	3	1.4 to 6.1	6.58	$\pmb{0}$	$\mathsf 0$	n/a
	Sed	20	20	4.6 to 9	9.38	$\pmb{0}$	0	100
Potassium	Qal	3	3	650 to 1700	2690	$\pmb{0}$	$\pmb{0}$	n/a
	Qbt 4	3	3	350 to 450	3500	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	1200 to 2000	2690	$\pmb{0}$	$\mathsf 0$	100
Selenium	Qal	$\ensuremath{\mathsf{3}}$	3	0.14 to 0.53	0.3	$\mathbf{1}$	0	n/a
	Qbt 4	3	3	0.08 to 0.11	0.3	$\pmb{0}$	$\pmb{0}$	n/a
	Sed	20	20	0.258 to 1.58	0.3	19	$\pmb{0}$	100
Silver	Qal	3	3	5.1 to 7.1	$\mathbf{1}$	3	0	n/a
	Qbt 4	3	$\mathfrak{S}$	$5.1$ to $6$	$\mathbf{1}$	$\mathbf{3}$	0	n/a
	Sed	20	20	1.3 to 2.2	$\mathbf{1}$	20	$\pmb{0}$	100
Sodium	Qal	3	3	150 to 220	1470	0	0	n/a
	Qbt 4	3	3	160 to 250	2770	0	0	n/a
	Sed	20	20	100 to 930	1470	0	0	100
Thallium	Qal	3	3	$0.2$ to $0.5$	0.73	$\mathbf 0$	0	n/a
	Qbt 4	3	3	0.17 to 0.2	1.1	0	0	n/a
	Sed	20	20	0.145 to 0.318	0.73	$\pmb{0}$	0	100

Chemical	Code Media	Number of Analyses	Number of <b>Detects</b>	Range (mg/kg) Concentration	(mg/kg) Σă	Number of ≧ <b>Detects</b> Above	Number of Non- Above Σñ <b>Detects</b>	Percent Detected for 20 Samples or Greater <sup>a</sup>
Uranium	Qal	3	3	0.46 to 0.76	2.22	$\mathbf 0$	$\mathbf 0$	n/a
	Qbt 4	3	3	0.35 to 0.43	2.4	$\mathbf 0$	$\mathbf 0$	n/a
	Sed	5	5	0.814 to 1.79	2.22	$\mathbf 0$	$\mathbf 0$	n/a
Vanadium	Qal	3	3	9.1 to 18	19.7	$\mathbf 0$	$\mathbf 0$	n/a
	Qbt 4	3	3	3 to 3.9	17	$\pmb{0}$	0	n/a
	Sed	20	20	9.1 to 36	19.7	$\mathbf{3}$	$\mathbf 0$	100
Zinc	Qal	3	3	31 to 32	60.2	$\mathbf 0$	$\mathbf 0$	n/a
	Qbt 4	3	3	36 to 39	63.5	$\mathbf 0$	0	n/a
	Sed	20	20	22 to 180	60.2	7	$\mathbf 0$	100

**Table 3.4-38 (continued)** 

*Sources*: LANL 1998, 59730 and EPA 1989, 08021.

a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less<br>than expected due to the inclusion of undetects not reported by this table.

than expected due to the inclusion of undetected by this table. But the inclusion of undetected by this table. But he absence of a background dataset for Qal, if available, Sed background values are assigned.

c<br>n/a = Not applicable.

d Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

e na = Not available.

260 outfall in reach CDV-1 East. These data are consistent with indications that the 260 outfall is the most important source for the barium outside of the active channel in Cañon de Valle. Also consistent with the screening sample data, barium concentrations are higher in the c3 and f1 units in reach CDV-2 West and CDV-2 East than in the c2 units; differences are greater in CDV-2 West than in CDV-2 East.

Trends in average barium concentration in active channel samples in Cañon de Valle from 1994 to 1996 differ from those in the fine-grained samples. Active channel sample concentrations are highest in reach CDV-1 East, upstream from the 260 outfall, with concentrations progressively declining downstream from this reach. Barium concentrations are much lower upstream in reach CDV-1 Central, although they are still above the sediment background (127 mg/kg) (LANL1998, 59730). These data therefore indicate the most important source for the barium present in the active stream channel prior to the Cerro Grande fire was upstream from the 260 outfall, specifically in the vicinity of MDA R, with additional sources existing upstream and downstream from this point.

The results support the existence of at least three sources of barium for the sediment in Cañon de Valle: (1) a minor source upstream from MDA R; (2) a larger source at, or in, the vicinity of MDA R, and the 260 outfall. Additional barium may have been contributed by erosion of soil at MDA P, but any contributions were apparently small enough that no impact on Cañon de Valle sediment could be identified from this source.

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#### **Table 3.4-39 (continued)**

\*See Appendix I-1 for further discussion.

Archival records and process knowledge indicate the 260 outfall is the primary source of barium in the watershed, which is consistent with the highest concentrations of barium occurring in sediment deposits downstream from the 260 outfall. However, the existence of higher average concentrations of barium in the active channel upstream from the 260 outfall rather than downstream in samples collected in 1994 to 1997 indicate in the recent past more barium was contributed from the area of MDA R than from the 260 outfall drainage. This may have been associated with a larger amount of erosion of contaminated soil at MDA R than along the 260 outfall drainage. This source has been reduced by the cleanup activities at MDA R following the Cerro Grande fire in 2000 (LANL 2001, 69971.2). The 260 outfall drainage also is expected to have been substantially reduced as a source following the IM (LANL 2002, 73706).

Concentrations of barium in the active channel deposits are higher (and a larger part of the barium inventory is present) (than in fine-grained sediment on adjacent abandoned channels and floodplains upstream from the 260 outfall. This pattern is reversed downstream. Without continued supply of barium from MDA R and the 260 outfall, concentrations in the active channel are expected to



#### **Table 3.4-40 Frequency of Detected Organic Chemicals in Martin Spring Canyon Alluvium, Sediment, and Tuff Samples**

*Source:* EPA 1989, 08021.<br>a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported b

than expected and the inclusion of undetection of units although some chemicals may be detected at values within this range.

 $c$ <sub>n/a</sub> = Not applicable.

decline over time, as will concentrations of barium contained within storm water or deposited on floodplains. Such decreases over time have been previously documented in other canyons at the Laboratory (e.g., Reneau et al. 1998, 59159; Reneau et al. 1998, 59160).

HMX was detected at relatively low concentrations upstream of the 260 outfall, and increases downstream from it, indicating the presence of a primary source at the 260 outfall. HMX is present at higher concentrations in fine-grained sediment than in the active channel in reach CDV-2 West, is higher in channel sediments in CDV-2 Central, and is at similar concentrations in these two facies in CDV-2 East. In reach CDV-2 West, HMX is higher in the c2 unit than in c3 and f1, which is the opposite of what was found for barium. This suggests differences in the timing of releases of these two chemicals, with the peak of HMX releases occurring after that of barium (under the assumption that fine-grained sediments deposited on the c2 unit are younger on average than in c3 and f1). Plots of HMX versus barium also indicate the absence of correlations between these two chemicals in both fine-grained samples and active channel samples (see Appendix E). The high average concentration of HMX in the active channel in CDV-2 Central is due to the influence of a single detected result that is anomalous relative to other active channel samples, and this average is therefore not considered reliable.



#### **Table 3.4-41 Retained and Eliminated Organic Chemicals in Martin Spring Canyon Alluvium, Sediment, and Tuff Samples**

RDX was detected upstream of the 260 outfall in both fine-grained sediment and in the active channel, indicating a source in the vicinity of MDA R and therefore, at least in part, a different source than the HMX source. In the fine-grained sediments, average concentrations of RDX are higher in CDV-1 East than in CDV-2 West, and progressively decrease downstream, although the CDV-1 East average is based on only two samples and may not be representative. The highest RDX value in fine-grained sediments was not detected in the same sample as the highest HMX value, suggesting an interference effect in the analysis and indicating the CDV-2 West average may be biased toward the high end. Average RDX concentrations in the active channel samples peak in CDV-2 West and decline downstream.

## Contaminant Inventory

Estimates of the inventory of barium, HMX, and RDX in fine-grained sediment in the different reaches of Cañon de Valle and Martin Spring Canyon were made using data on the area, density, average thickness of fine-grained sediment, and average contaminant concentration in each unit. Sediment density was assumed to be the same as the density of texturally similar sediment in Los Alamos and Pueblo Canyons (Reneau et al.1998, 59159; Reneau et al. 1998, 59160). An estimate of the inventory in reach CDV-2 Central was based on data from adjacent reaches, assuming unit thicknesses and contaminant concentrations for each unit were averages of values in CDV-2 West and CDV-2 East. These estimates are based on a relatively small number of samples per unit, and associated uncertainties are therefore higher than if a larger data set were available. However, because the samples submitted for analysis were selected based on a larger number of screening samples, the general magnitudes and spatial trends are considered to be reliable.



An estimate of the total inventory of barium in Cañon de Valle sediment was made by using available data and extrapolating to non-sampled reaches. Based on the data from active channel samples, it was assumed the same average concentrations present in reach CDV-2 East persist for an additional 2755 ft downstream (reach "CDV-2 East+"), and that barium is essentially at background farther downstream (reach "CDV-2 East++") and can be excluded from the inventory calculations. It is also assumed that characteristics of geomorphic units (average width and thickness) downstream from CDV-2 East are the same as in that reach. A total of about 21,000 kg of barium is estimated to have been in Cañon de Valle sediment before the Cerro Grande fire, roughly half upstream from MDA P and half downstream. It is estimated that about 62% is stored in fine-grained sediment deposits outside the active channel, about 10% is stored in the active channel, and the remainder is stored in coarse-grained deposits in abandoned channel units.

Resampling of a subset of the 1996 active channel locations in 2002 allows a comparison of barium concentrations in the channel 6 years after the termination of effluent releases from the 260 outfall. This period also includes the effects of post-fire floods. In reaches CDV-1 East and CDV-2 West, barium concentrations in 2002 were much lower than in 1996. This suggests that much of the barium present in the active channel in these reaches in 1996 was scoured and suspended in subsequent floods and transported downstream, depleting the active channel inventory. The amount that was redeposited on abandoned channels and floodplains is unknown. It is notable that concentrations measured in 2002 are similar in reaches CDV-1 East, CDV-2 West, and CDV-2 East, and are also similar to those occurring in reaches CDV-2 East and CDV-2 East+ in 1996.

Estimates of the total inventory of HMX and RDX in Cañon de Valle sediments before the Cerro Grande fire are roughly 50 kg of HMX (half in fine-grained sediment and coarse-grained sediments) and roughly 5 kg of RDX (about 60% in fine-grained sediments).

In all cases, average concentrations of HMX and RDX in active channel samples (except for RDX in reach CDV-2 East) have much lower concentrations in 2002 than in 1996. These data therefore support the inference made from barium data that much of the contaminant inventory stored in the active channel in 1996 was remobilized and transported downstream prior to 2002, either in post-fire floods or in other storm runoff events.

# **3.4.2.6 Results of Ecological Risk Assessment Sampling**

There are sediment and water data associated with the toxicity testing previously described in this section. The benthic macro-invertebrate data are produced by the NMED Oversight Bureau. Those data are presented in NMED (1999, 73769), Ford-Schmid (1998, 73772), and NMED (2003, 76072). The reader is referred to those documents for additional information.

## **3.4.2.6.1 Toxicity Testing:** *Chironomus tentans* **Survival and Growth**

Table 3.4-42 presents the results for survival and growth for the two rounds of testing of *Chironomus tentans* used in the baseline ecological risk assessment. Sample locations are shown on Figure 3.3-10. The first set of results includes all four locations tested (including the reference site in Starmer's Gulch). The second set of results includes two sediment samples for Location ID 16-06709 near SWSC Cut. One sediment sample was tested using site water for static renewal. The other sediment sample was tested using reconstituted laboratory water for static renewal. The second round of testing did not include the Location ID 16-06711 downstream of MDA P. The analysis and assessment of these data, comparing the reference site to areas with likely contaminants, is presented in Appendix L.

<b>Sample</b> ID	Location ID	<b>Sampling</b> <b>Date</b>	<b>Site</b> Water	<b>Mean Percent</b> <b>Survival</b>	<b>Mean Growth</b> (mg ash-free dry weight)
RE16-01-3283	16-06709	9/21/2001	Yes	22.50	0.68
RF16-01-3285	16-06710	9/22/2001	Yes	68.75	0.38
RE16-01-3287	16-06711	9/23/2001	Yes	86.25	0.39
RF16-01-3289	16-06712	9/24/2001	Yes	82.50	0.44
RE16-03-49883	16-06709	12/6/2002	Yes	90.00	1.28
RE16-03-49885	16-06709	12/7/2002	No.	91.25	0.89
RE16-03-49884	16-06710	12/8/2002	Yes	88.75	1.26
RE16-03-49886	16-06712	12/9/2002	Yes	96.25	1.21

**Table 3.4-42**  *Chironomus tentans* **Toxicity Testing Results for Survival and Growth** 

## **3.4.2.6.2 Small Mammal Whole-Body Burden Results**

A total of 31 small mammals were submitted for contaminant analysis. A summary of the sample identification numbers, collection dates, locations, and the analytical request numbers is provided in Appendix G-1. Thirty of the samples are field-caught small mammals. The quality control animal was purchased from a biological materials supplier and is used as a blank and for spikes to assess laboratory performance.

Table 3.4-43 presents the frequency of detected inorganic chemicals in the 30 field-caught small mammals. No table is provided for HE because all of the results were undetected. The analysis and interpretation of these data relative to potential contaminant doses to the Mexican spotted owl is provided in Appendix L.

## **3.4.3 Summary of Findings and Implications for the Conceptual Model**

This section provides a summary of findings for Cañon de Valle and Martin Spring Canyon alluvial systems, including identified COPCs, hydrogeological and geochemical dynamics, and important observations regarding the distribution and inventory of contaminants, including uncertainties. Section 5.0, Conceptual Model, provides further integration of the new findings into the existing site data and knowledge base.

Table 3.4-44 provides a summary of the COPCs for all media in Cañon de Valle and Martin Spring Canyon. Maps of barium and RDX concentration in water and sediment are shown in Figures 3.4-27 through 3.4-34. These figures present both the most recent concentration value and the maximum concentration for each sampling point location collected from 1998 to 2002. Significant findings for Cañon de Valle and Martin Spring Canyon are described below.

## Hydraulic Connectivity

• The alluvial groundwater in Cañon de Valle appears to be connected throughout the saturated alluvium. However, differing head responses in the monitoring wells indicates heterogeneity within the alluvium. Each of the four alluvial wells in the canyon bottom appears to have fairly

distinct well-level responses to precipitation and snowmelt inputs. This implies there is weak horizontal connectivity throughout the canyon bottom alluvial system.

- Barium concentrations are consistently higher in the alluvial groundwater than in the surface water. One explanation for this is that a secondary source of barium resides within the alluvium. The implication is that the exchange of surface water and alluvial groundwater can occur, but is localized.
- Oxygen isotope results show the alluvial groundwater and the surface water do not always follow the same trends, indicating there are source differences between surface and alluvial groundwater (even though there is exchange between the two).
- There are losing and gaining reaches in Cañon de Valle. The water lost may move into storage in the alluvium or represent a source for recharge to the more deeply perched groundwater. Gaining areas, such as the seep at SP#13, could represent an additional source of contamination to the surface water system.
- The time series results for the alluvial groundwater oxygen isotopes show the peaks and valleys are not of the same magnitude and do not occur at the same time. This further indicates the lack of homogeneity within the canyon bottom alluvial system.
- HRR geophysical surveys show a highly conductive region below the Burning Ground Spring wetland area. HRR geophysical surveys also shows an approximately 20-ft-thick low resistance layer, dipping to the west, approximately 200 ft upstream from MDA P. This could be one potential zone of deeper infiltration from the alluvial system.
- CSAMT/NSAMT geophysical surveys conducted to 1500 ft bgs indicate the presence of discrete heterogeneous subvertical, electrically-conductive layers. The deep conductive zone appears to be bounded on the east and may be discontinuous in nature. The conductive zone may represent preferential pathways such as surge beds or fracture zones. A follow up survey is planned in late 2003 to provide greater resolution.

#### Alluvial System Dynamics—Cañon de Valle

- RDX concentrations in the surface water and alluvial groundwater in Cañon de Valle are highest near the 260 outfall area. The highest mass flow rate of RDX in surface water occurred during wet periods.
- The lowest concentration of barium in the alluvial groundwater was observed in upstream Well 16-02655, followed by Well 16-02656, and Well 16-02659. The highest barium concentration was observed in Well 16-02658. Figures 3.4-29 and 3.4-30 show the maximum and most recent barium concentrations, respectively, in Cañon de Valle surface water and alluvial groundwater.
- Both barium and RDX were detected in surface water samples at the confluence with Water Canyon (approximately 3 mi downstream of the source area). This indicates the entire Cañon de Valle alluvial system contains barium and RDX.
- RDX concentrations for Well 16-02659 (located the farthest distance east from the 260 outfall) were consistently higher than Wells 16-02655, 16-02656, and 16-02658 (see Figure 3.4-27). There is no trend of decreasing RDX concentrations with distance from the 260 outfall.

Figure 3.4-27 and 3.4-28 show the maximum and most recent RDX concentrations, respectively in Cañon de Valle surface and alluvial groundwater.

- Barium concentration trends in alluvial groundwater over time are stable to slightly decreasing. Spikes associated with pulses of barium into the system are possibly due to sediment flushing. There does not appear to be a significant correlation between barium concentrations and saturated thickness. No evidence of an effect or reduction in barium concentration related to the IM source removal action is yet apparent.
- There is a positive correlation between variations in saturated thickness in Cañon de Valle alluvial wells and RDX concentration, indicating RDX residing within the vadose zone constitutes an important secondary source and is released to the alluvial groundwater during periods of increased saturated thickness in the alluvium. It may be difficult to define the extent of this secondary source within the unsaturated zone.

#### Alluvial System Dynamics—Martin Spring Canyon

- RDX was detected in the surface and alluvial groundwater at locations in Martin Spring Canyon. Groundwater discharge from Martin Spring and the K-Site drop tower could be the primary sources for RDX in the canyon. Figures 3.4-27 and 3.4-28 show the maximum and most recent RDX concentrations, respectively, in Martin Spring Canyon surface and alluvial groundwater.
- The concentrations of RDX and barium were generally lower in Martin Spring Canyon than in Cañon de Valle. There are samples that contained higher concentrations of barium in single locations. For instance, high concentrations of barium in surface water are detected at Location ID 16-05988, (SP#3 in Martin Spring Canyon) in July 1999, and in the alluvial groundwater from Well 16-06295 (Well #3 MSC) in September 2000. A possible explanation for this is the intermittent release of stored contaminants from the surface or vadose zone.

#### Alluvial Sediment Dynamics—Cañon de Valle

- The geomorphic investigation results support the existence of at least three sources of barium for the sediment in Cañon de Valle: (1) a minor source upstream from MDA R, possibly SWMU 16-026(m), the outfall for the 90s Line building; (2) a larger source at, or in the vicinity of, MDA R; and (3) the 260 outfall. Figures 3.4-31 and 3.4-32 show the most recent concentrations of RDX and barium, respectively, in Cañon de Valle sediment.
- Resampling of a subset of the 1996 active channel locations in 2002 allowed a time comparison of barium and RDX concentrations. For barium, concentrations were noticeably lower in the reaches immediately upstream and downstream of the 260 outfall. For RDX, all reaches had lower concentrations in 2002, except the reach downstream of Well 16-02658. The decrease in RDX concentrations may be due to elimination of discharges or increased channel flows and subsequent transport of contaminated sediment outside the study area following the 2000 Cerro Grande fire.
- Approximately 5 kg of RDX was estimated to reside in Cañon de Valle sediment before the 2000 Cerro Grande fire. A total of about 21,000 kg of barium is estimated to have been in Cañon de Valle sediment before the Cerro Grande fire, roughly half of which was upstream from MDA P and half of which was downstream.
- Immediately down canyon from Location ID 16-05967, (Silver Seep), screening data reported silver concentrations of 2595 and 957 mg/kg. Within the main reach of Cañon de Valle, 40 out of 46 samples exceed the 1.0 mg/kg sediment BV for silver (LANL 1998, 59730).
- Alluvial sediment within the Cañon de Valle contains metals, HE, PAHs, and SVOCs. These samples were collected between 1 and 2 ft below grade. The vertical extent of vadose zone contamination below this horizon is unknown.

#### Alluvial Sediment Dynamics—Martin Spring Canyon

• Barium and RDX are both present in Martin Spring Canyon, but at much lower concentrations and with much smaller inventories than in Cañon de Valle. Figures 3.4-33 and 3.4-34 show the most recent concentrations of RDX and barium, respectively, in Martin Spring Canyon.

The source for barium in Martin Spring Canyon sediment is located somewhere up the tributary drainage east of TA-16 HE casting building 306, and concentrations decline downstream, as mixing with sediment sources occurs.



# **Table 3.4-43**

#### **Frequency of Detected Inorganic Chemicals in Whole Body Small Mammal Analysis**

## **Table 3.4-43 (continued) Frequency of Detected Inorganic Chemicals in Whole Body Small Mammal Analysis**



*Source:* EPA 1989, 08021.<br><sup>a</sup> The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less

than expected due to the inclusion of undetects not reported by this table.<br><sup>D</sup> Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

c<br>n/a = Not applicable.



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Rubidium

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Table 3.4-44 (continued) **Table 3.4-44 (continued)**

**3.4-41)** 

**MSC Quaternary Alluvium (Qal) (see Tables 3.4-39 and 3.4-41)** 

 $\mathcal{I}$ l.  $\mathbf{I}$  $\mathbf{I}$  $\overline{\phantom{a}}$  $\begin{array}{c} \hline \end{array}$ 

Dinitrobenzene[1,3-]

Dinitrobenzene[1,3-] ● — — — — — — —

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 $\overline{\phantom{a}}$ 

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 $\overline{\phantom{a}}$  $\overline{\phantom{a}}$  $\overline{\phantom{a}}$ 



Table 3.4-44 (continued)

*Phase III RFI Report* 

**Tables 3.4-39 and 3.4-41)** 

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- Chemical was analyzed for but eliminated as a COPC for this alluvial system component.  $a$  — = Chemical was analyzed for but eliminated as a COPC for this alluvial system component.

 $\begin{array}{c} \end{array}$  $\bullet$ 

Trinitrotoluene[2,4,6-]

 $\sigma$ م

Trinitrotoluene[2,4,6-] ● ● ● — — ● — —

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 $\bullet$  = Chemical retained as a COPC for this alluvial system component.  $\mathbf{b}$   $\bullet$  = Chemical retained as a COPC for this alluvial system component.

 $c<sub>NA</sub>$  = Not analyzed.  $C_{NA}$  = Not analyzed.

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- -
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	-
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- 837 Spring RDX Concentration (μg/L)
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**Figure 3.4-27. Maximum concentrations of RDX in Cañon de Valle and Martin Spring Canyon surface water, alluvial groundwater, springs, and seeps** 

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**Figure 3.4-28. Most recent concentrations of RDX in Cañon de Valle and Martin Spring Canyon surface water, alluvial groundwater, springs, and seeps** 

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**Figure 3.4-29. Maximum concentrations of barium in Cañon de Valle and Martin Spring Canyon surface water, alluvial groundwater, springs, and seeps** 

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**Figure 3.4-30. Most recent concentrations of barium in Cañon de Valle and Martin Spring Canyon surface water, alluvial groundwater, springs, and seeps** 

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**Figure 3.4-33. Most recent concentrations of RDX in Martin Spring Canyon sediment** 



**Figure 3.4-34. Most recent concentrations of barium in Martin Spring Canyon sediment** 

## **4.0 SUBSURFACE SYSTEM INVESTIGATION**

### **4.1 Summary**

This section describes the subsurface hydrogeology investigation of Cañon de Valle and Martin Spring Canyon. This investigation was outlined in detail in the CMS plan for SWMU 16-021(c)-99 (see sections 6.1.3 and 6.3.3 in LANL 1998, 62413.3) and in previous RFI reports submitted in 1996 and 1998 (LANL 1996, 55077; LANL 1998, 59891).

Investigation of the subsurface hydrogeology for SWMU 16-021(c)-99 is divided into three categories:

- The chemical characterization of springs
- The intermediate-depth (less than 210 ft) perched aquifer investigation
- The 90s Line Pond investigations

See Figures 4.1-1 through 4.1-4 for photographs of the springs and 90s Line Pond.

Spring investigations are included in this section because the springs are a manifestation of the intermediate-depth perched aquifer that underlies the northwestern portion of TA-16. The 90s Line Pond was included as this may be a recharge source affecting both the springs and the intermediate-depth perched aquifer.

The principal goals of these investigations are (1) to better understand the transport pathways that connect the 260 outfall [the source region for SWMU 16-021(c)-99] with the intermediate-depth perched groundwater and (2) to better understand the dynamics, residence times, and contaminant concentrations of the intermediate-depth perched aquifer at TA-16 that discharges at the springs.

The intermediate-depth perched aquifer investigation included drilling five boreholes to depths from 91 to 207 ft and installing wells at locations likely to intersect the perched saturated zones at TA-16 (Figure 4.1-5). These wells include Well 16-02665 in Martin Spring Canyon, Well 16-02667 within SWSC Cut, Well 16-02668 near Building 300, and Well 16-02669 located east of the 90s Line Pond. A fifth well, (Well 16-02712) was located in the Cañon de Valle upper drainage channel, downstream of the former settling pond. This well was plugged and abandoned during the IM in 2000. Detailed geologic core logs of lithologic units and well construction diagrams for these five wells are provided in the Phase II RFI report (LANL 1998, 59891). The core logs of these wells indicate flat-lying subunits, except near Cañon de Valle. The local trend of subunit-subunit contacts is to the north and east.

The intermediate-depth perched aquifer is ephemeral in most of the well locations. Analysis of this perched aquifer indicates low levels of contamination. These wells wet up infrequently but, when wet, contaminant levels for several constituents, including HE, exceed screening limits. The Martin Spring Canyon well (Well 16-02665) contained water the most frequently of the five during this investigation. Inorganic COPCs include aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, and zinc. Organic COPCs with significant detections include HMX and RDX. Aluminum, boron, manganese, and RDX are the most common COPCs affecting Wells 16-02665, 16-02669, and 16-02712 (prior to abandonment), with the highest values observed at Well 16-02712. Similarities in chemistry between Well 16-02665 and Martin Spring (e.g., for boron) indicate a similar hydraulic zone and contaminant source. The spring investigation relevant to the subsurface hydrogeology included quarterly sampling of the three springs identified in and around this area of TA-16; SWSC Spring, Burning Ground Spring, and Martin Spring (Figure 4.1-5). Additional flow-integrated samples were also collected. Analytical data from these sampling campaigns indicate all three springs contain RDX and TNT as COPCs. Other significant inorganic COPCs include

barium and boron (Martin Spring only). RDX, TNT, barium, and boron are almost certainly associated with TA-16 operations.



**Figure 4.1-1. Field personnel conducting monthly maintenance at Martin Spring. Several instruments are deployed at this location. Flow rate, temperature, and conductivity measurements are collected hourly. In the background, there are two stormwater filters which are designed to filter barium and RDX from the spring effluent. View is down-canyon to the east. Photo was taken in November 2002.** 



**Figure 4.1-2. SWSC Spring V-notch weir. SWSC Spring has been dry since December 2001. Photo was taken June 2002.** 



**Figure 4.1-3. Burning Ground Spring** 



**Figure 4.1-4. Field team member collecting water sample from Location ID 16-05826, 90s Line Pond. Photo was taken in June 2002. View is to the northwest.** 



Time-series analysis of the spring concentration data indicates extreme variability in the concentrations of constituents (up to three orders of magnitude for several COPCs such as aluminum and iron). There is little evidence of seasonality or trends in contaminant concentration over time, though some exceptions do exist. For example, barium, nitrate, iron, and lead concentrations in unfiltered samples from Burning Ground Spring appear to be decreasing over time. Martin Spring appears to have a distinct chemistry relative to SWSC Spring and Burning Ground Spring. Martin Spring has higher concentrations of several inorganic chemicals than SWSC and Burning Ground Springs, including boron, nitrate, and RDX and has the lowest RDX/HMX ratio, which indicates it might be affected by contamination from a source other than the 260 outfall. SWSC Spring and Burning Ground Spring have chemistries that are more similar. Flow rate changes during the pre-1998 period indicate SWSC Spring and Burning Ground Spring are hydrogeologically similar, but that Martin Spring probably represents a different hydrogeologic system. Since drought conditions began in 1998, SWSC Spring has dried up while Burning Ground Spring has continued flowing. The mass of barium and RDX at Martin Spring has been increasing over time, while the mass of barium at Burning Ground Spring appears to be decreasing over time. The increases at Martin Spring may represent (1) the center of mass of a contaminant plume approaching the spring or concentration of flow in more contaminated portions of the vadose zone, (2) changes in the relative contribution of fast versus slow recharge pathways, or (3) desorption of contaminants from solid bound phases during drought periods. The decreases in barium at Burning Ground Spring may be a function of decreased base flow and/or flow having been concentrated in well flushed regions of the hydrologic system during drought periods. Flow rate appears to be a major control over the concentrations of barium and RDX at Martin Spring, with increased flow leading to a dilution effect. At SWSC Spring, increased (when water present) flow leads to increased RDX concentrations. The same is true of barium at Burning Ground Spring. These latter two relationships indicate a flushing effect, perhaps related to flushing of macropores containing contaminant concentrations.

The 90s Line Pond has wetted up periodically during the study period as a result of precipitation/ snowmelt events. COPCs include aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, selenium, thallium, uranium, vanadium, and RDX. Of these, aluminum, barium, lead, manganese, and RDX most commonly exceed water quality screening levels. Many of these COPCs have higher concentrations in the pond relative to the springs, particularly in unfiltered samples.

## **4.2 Data Needs and Objectives**

Phase I and II RFIs at SWMU 16-021(c)-99 demonstrated elevated levels of contaminants in the 260 outfall and identified contamination in surface water and spring water at TA-16 (LANL 1996, 55077; LANL 1998, 59891). The CMS plan for SWMU 16-021(c)-99 (LANL 1998; 62413.3, section 6.3.3) provided a subsurface system investigation portion of the Phase III sampling and analysis plan (SAP). The main issues addressed by the Phase III SAP include (1) identifying the groundwater pathways, if any, which connect the 260 outfall (or other source areas) to TA-16's intermediate-depth perched aquifer, seeps, and springs associated with the 260 outfall, (2) assessing residence times and contaminants concentrations in the springs, and (3) determining spring dynamics.

The issues noted above are addressed by focused investigations designed to (1) answer questions concerning the hydrologic connectivity between the 260 outfall and the springs, (2) examine the connection between other potential contaminant sources and the springs, (3) identify COPCs in the intermediate-depth perched aquifer which might require remediation, (4) assist with the location selection of potentially long-term monitoring wells, (5) help design a systematic monitoring system, and (6) gather contaminant data to support CMS remedy selection at the site.

To evaluate the data collected during the subsurface investigation, the following decision points and corresponding actions are identified.

- If the saturated pathways connecting the 260 outfall to the springs are identified and if they contain constituents at levels greater than MCLs, then implement groundwater monitoring in those pathways.
- If the saturated pathways connecting the 260 outfall to the springs are not identified, then examine other TA-16 discharge areas associated with other SWMUs as potential sources (LANL 1996, 55077, p. 59–61).
- If the 260 outfall is shown to contribute constituents to the intermediate-depth perched aquifer and if those constituents present a potential current or future risk to human health and the environment, then evaluate appropriate alternatives within the context of the CMS.

#### **4.3 Scope of Sampling and Analysis**

The scope of the subsurface investigation includes characterization of the intermediate-depth perched aquifer in the five intermediate-depth wells (to a maximum depth of approximately 207 ft) and in the three springs. The intermediate-depth wells include Well 16-02665, Well 16-02667, Well 16-02668, Well 16-02699, and Well 16-02712. The three springs investigated are Burning Ground Spring and SWSC Spring in Cañon de Valle and Martin Spring in Martin Spring Canyon. Surface water in the 90s Line Pond is also included due to its potential connectivity to the intermediate-depth perched aquifer and with the springs.

In December 1999 Martin, Burning Ground, and SWSC Springs were each instrumented with a flow logger and an autosampler to take weekly flow-integrated samples of spring discharge. The flow logger measured discharge and signaled the autosampler to sample. The autosamplers sampled as a function of discharge (i.e., 20 mL of water would be collected after every 150 L of discharge). The sample volumes (20 mL) and sample interval volumes (150 L) were individually determined for each spring because of the differing flow regimes. The sample interval volume had to be set such that during periods of low flow, the 5-L minimum would be met and during periods of high flow, the 12- or 24-L storage capacity of the sampler would not be exceeded. Weekly, the autosamplers would sample 100–500 times collecting the 20- to 50-mL volumes required such that the minimum of 5 L of water could be collected. The sample volume and sample interval volume values were adjusted several times during the study period because of seasonal fluctuations in flow. Flow-integrated samples were collected at the end of each week. Samples were submitted only when all three samplers continuously collected samples and a representative weekly flow regime could be obtained. Field-screening parameters were taken of spring water at collection time. Flow-integrated sampling began in January 2000. A total of 50 weekly flowintegrated samples and 6 flow-integrated composite monthly samples from each spring were collected each year. Eight of the 15 weekly flow-integrated samples and all 6 of the monthly flow-integrated samples were sent for analytical laboratory analyses. Samples were analyzed for HE compounds, metals, major anions and cations, and bicarbonate, with the exception of the monthly composite samples for which HE were not to be analyzed due to holding time exceedance. Daily flow data and other parameters, including temperature and conductivity, were collected at each spring. pH was monitored monthly. Quarterly grab samples for HE, VOCs, SVOCs, and inorganic chemicals were collected from the springs, the intermediate-depth perched aquifer wells, and 90s Line Pond when sufficient water was present.

In addition, water samples for stable isotope analysis were collected every other day with auto-samplers at the three springs. Submission of isotope samples was at an approximate rate of 1 in 10 during stable atmospheric periods and 1 in 4 during seasonal transitions (e.g., snowmelt, monsoon, etc.). At least

25  $\delta^{18}$ O samples per year, except at SWSC Spring where  $\delta^{18}$ O was discontinued in 2000, were analyzed under this scheme. Samples for  $\delta$ D and  $\delta^{15}$ N were collected as part of the quarterly sampling starting in 1999. Isotopic samples from 90s Line Pond and Well 16-02665 were also collected when water was available.

Sample collection and handling conformed to the following plans, procedures, and Laboratory implementation requirements (LIRs):

- Phase I and II RFI reports for TA-16, SWMU 16-021(c)-99 (LANL 1996, 55077; LANL 1998; 59891), and the CMS plan for SWMU 16-021(c)-99 (LANL 1998, 62413.3) except for deviations discussed in more detail below
- Site-Specific Health and Safety Plan
- OU 1082 Waste Management Plan
- OU 1082 Quality Assurance Plan (LANL 1996, 54609)
- Data Quality Objectives and Sampling and Analysis Plans for Additional and/or Modified Sampling at OU 1082
- LANL-LP 116-1.0, Stop Work and Restart
- LANL-ER-SOP-1.01, General Instructions for Field Investigations
- LANL-ER-SOP-1.02, Sample Containers and Preservation
- LANL-ER-SOP-1.03, Handling, Packaging, and Shipping of Samples
- LANL-ER-SOP-1.04, Sample Control and Field Documentation
- LANL-ER-SOP-1.05, Field Quality Control Samples
- LANL-ER-SOP-1-06, Management of RFI-Generated Waste
- LANL-ER-SOP-1.07, Operational Guidelines for Taking Soil and Water Samples in Explosive Areas
- LANL-ER-SOP-1.08, Field Decontamination of Drilling and Sampling Equipment
- LANL-ER-SOP-4.01, Drilling Methods and Drill Site Management
- LANL-ER-SOP-4.04, General Borehole Logging
- LANL-ER-SOP-5.01, Monitor Well Construction
- LANL-ER-SOP-5.02, Well Development
- LANL-ER-SOP-6.09, Spade and Scoop Method for Collection of Soil Samples
- LANL-ER-SOP-6.10, Hand Auger and Thin-Wall Tube Sampler
- LANL-ER-SOP-6.24, Sample Collection from Split-Spoon Samplers and Shelby Tube Samplers
- LANL-ER-SOP 10.06, High Explosives Spot Test
- LANL-ER-SOP-12.01, Field Logging, Handling, and Documentation of Borehole Materials
- LANL-ER-SOP-12.02, Transportation, Receipt, and Admittance of Borehole Samples to the Sample Management Facility
- LANL-ER-SOP-12.03, Acceptance of Non-borehole Samples by the Sample Management Facility
- LIR 402-820-01, Noise and Temperature Stresses
- LIR 402-1000-01, Personal Protective Equipment
- LANL Administrative Requirement 15-1, Field Work
- LANL-ER-QAPjP-06, Sampling Procedures
- LANL-ER-QAPjP-07, Sample Custody
- LANL-ER-QAPjP-08, Calibration Procedures and Frequency

The Cerro Grande fire of May 2000 interrupted the normal sampling schedule. Following the fire, many additional samples were collected in order to assess the impact of the fire on water chemistry. Fewer flow-integrated samples were sent out for laboratory analysis due to the prevalence of a drought-related low flow regime (typically five to six weekly flow-integrated samples were sent out per year for laboratory analysis and only one to two monthly flow-integrated samples were sent out for analysis in 2000; monthly flow-integrated samples were measured for HE). Due to the Cerro Grande fire, sampling was extended an additional 18 months, ending in 2002 rather than in 2000. Samples were not analyzed for certain anions, including chloride, from approximately August 2001 until June 2002 due to temporal similarity of the chemical data. The discontinuance of monitoring was approved by the NMED. SWSC Spring was not analyzed when dry (see section 4.4.2.1.8).

#### **4.4 Results**

### **4.4.1 Analytical Data Quality Assessment**

All analytical samples were sent for fixed-laboratory analysis at offsite commercial analytical laboratories. All analytical results received routine data validation, with some results receiving focused validation as necessary. Validation results for all analytical data are summarized in Appendix F and indicate that the data set is of sufficient quantity and quality to be used in data analysis, including risk assessment.

#### **4.4.2 Analytical Data Presentation**

The following sections present water quality data and screening parameters for the springs, the 90s Line Pond, and the intermediate-depth boreholes.

## **4.4.2.1 Spring/Pond Quarterly Sampling and Spring Dynamics**

This section provides data from three springs located at TA-16; SWSC Spring, Martin Spring, and Burning Ground Spring (Figure 4.1-5). Data in this section include quarterly sampling data and flow-integrated sampling data collected between March 1998 and July 2002. Data from the Phase II RFI report (LANL 1998, 59891) are not included in data tables, but are included in graphs used for interpretation. All analyses were completed with EPA SW-846 methods when available. Both filtered and unfiltered samples were collected. For most analytes, the differences between filtered and unfiltered samples are small, with the exception of some metals such as iron and aluminum. For purposes of interpreting the relevance of the data to the site-wide conceptual model, the focus was on seven analytes: barium, RDX, perchlorate, nitrate + nitrite, calcium, chloride, and iron. This suite represents four contaminants (barium, RDX, perchlorate, and nitrate + nitrite), a major cation (calcium), a major anion (chloride), and a metal (iron) that is redox sensitive and prone to colloidal transport. Whereas other COPCs have been identified in addition to the four focused on here, the other COPCs typically only exceeded screening limits on a few occasions. In addition, some chemicals are strongly correlated (e.g., aluminum and iron; see Figures 4.5-3c, 4.5-3f, 4.5-3i). The screening process for the identification of COPCs is described in section 1.5. Unless otherwise noted, all figures in this section refer to unfiltered water data. Only iron is

separated out into filtered and unfiltered samples for the purpose of time-series and other data analysis. The chemistry of flow-integrated samples was compared with that of quarterly grab samples for barium, calcium, chloride, iron, and RDX. For comparisons to be made, collection dates had to be within ten days of one another and data to be compared could not be qualified as J or U. In order to make the most rigorous comparisons, J- qualified data were omitted from the analysis. In addition, J+ qualified data were also omitted for flow-integrated samples so that they were not compared with qualified numbers from grab samples, subsequently providing a false impression that flow-integrated values were significantly higher. In most cases, the flow-integrated samples have higher concentrations of barium, calcium, chloride, iron, and RDX than quarterly grab samples, though several exceptions are found. For unfiltered samples, the concentration differences (where flow-integrated concentrations were higher than quarterly grab sample concentrations, a positive value is presented, whereas flow-integrated concentrations less than quarterly sample concentrations represents a negative value) averaged over all comparable time periods and across all 3 springs are approximately 13% for barium, 10% for calcium, 7% for chloride, 116% for iron, and -1% for RDX. Fewer comparisons are available for filtered samples, but absolute differences average 5% for barium and 4% for calcium. These differences are small compared to the total temporal variability in the data sets. Flow-integrated and quarterly grab samples are not separated for the purpose of statistical data analysis.

# **4.4.2.1.1 Springs—Evaluation of Inorganic Chemicals**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of detected inorganic chemicals is provided in Table G-2.19 (located in Appendix G-2). Complete analytical data for inorganic chemical analyses of spring water are provided in Appendix G-3. QA/QC assessment results for these data are summarized in Appendix F. The lack of a background data set with which to compare spring data presented a difficultly in analyzing the data from the TA-16 springs. A geochemical analysis comparing naturally occurring concentrations of inorganic chemicals was performed to augment the lack of BVs for springs (see Appendix I-2). Data are subsequently screened against NMWQCC numeric groundwater standards, EPA MCLs, and Region 6 tap water PRGs. This screening process is described in section 1.5. Frequency of detected inorganic chemicals, screening results, and retained and eliminated tables for inorganic chemicals in the springs are shown in Tables 4.4-1, 4.4-2, and 4.4-3, respectively.

Analyses were conducted for inorganic chemicals in all springs to identify sources of spring water, including anthropogenic sources. Analysis of these various chemicals can provide clues as to the sources of water supporting spring flow, and temporal changes in these chemicals can provide information on the dynamics of the saturated system feeding the springs. The following inorganic chemicals were retained as COPCs; antimony, barium, boron, cesium, cyanide, mercury, nitrate + nitrite, perchlorate, rubidium, thallium, and uranium. Barium and boron are the most prevalent COPCs, based on the frequency of detection. As stated previously, the interpretation of inorganic chemicals relative to spring dynamics will focus on barium, calcium, chloride, iron, nitrate + nitrite, and perchlorate. Trend plots for these elements are shown in Figures 4.4-1a–c for barium and in Appendix I-3 (Figures I3-1 through I3-6, I3-14 through I3-19, and I3-27 through I3-32) for the other chemicals. For all statistical analyses, the significance level has been chosen to be p = 0.05. For nitrate + nitrite plots, two very high values have not been plotted for both Martin Spring and SWSC Spring. While these points have been through quality analysis, it is suspicious that they are exactly three orders of magnitude higher relative to the rest of the data set, indicating a potential units issue that has not been identified in laboratory data packages. In any case, temporal trends are not statistically significant whether these points are included or not.

<b>Chemical</b>	<b>Field</b> Preparation	<b>Analyses</b>	Number of Number of <b>Detects</b>	<b>Concentration</b> Range (µg/L)	<b>Percent Detected</b> for 20 Samples or Greater <sup>a</sup>
Aluminum	Filtered	$\overline{96}$	51	[7.6] <sup>b</sup> to 5130	70
	<b>Unfiltered</b>	101	87	$[12.\overline{6}]$ to 17100	
Antimony	Filtered	93	18	$[0.139]$ to $[20]$	16
	Unfiltered	98	13	0.05 to [20]	
Arsenic	Filtered	95	24	$[0.14]$ to $[5]$	28
	<b>Unfiltered</b>	100	30	$[0.14]$ to 10.1	
<b>Barium</b>	Filtered	94	94	112 to 914	100
	<b>Unfiltered</b>	99	99	125 to 1310	
Beryllium	Filtered	96	9	$0.01$ to [4]	15
	<b>Unfiltered</b>	101	20	$0.01$ to [4]	
Boron	Filtered	96	74	4.01 to 2840	76
	Unfiltered	98	74	3.35 to 2750	
Cadmium	Filtered	96	24	$0.05$ to $[5]$	25
	<b>Unfiltered</b>	101	25	$\overline{0.01}$ to [5]	
Calcium	Filtered	96	96	14000 to 42800	100
	<b>Unfiltered</b>	101	101	13000 to 44000	
Cesium	Filtered	3	1	500 to 500	n/a <sup>c</sup>
	<b>Unfiltered</b>	$\overline{3}$	$\mathbf 0$	[500 to 500]	
Chloride	Filtered	$\overline{9}$	9	12000 to 23000	100
	Unfiltered	87	87	9660 to 32000	
Chromium	Filtered	96	55	[0.21] to 29.3	60
	<b>Unfiltered</b>	101	64	[0.37] to 32.7	
Cobalt	Filtered	96	33	$[0.17]$ to $[20]$	27
	Unfiltered	101	$\overline{21}$	0.0882 to [20]	
Copper	Filtered	96	22	$[0.27]$ to $[20]$	32
	<b>Unfiltered</b>	101	41	[0.27] to 43.1	
Cyanide (Total)	Filtered	6	$\pmb{0}$	[2.5 to 13]	n/a
	Unfiltered	$\overline{6}$	1	3.2 to [10]	
Fluoride	Filtered	$\overline{9}$	$\boldsymbol{9}$	160 to 670	99
	<b>Unfiltered</b>	$\overline{87}$	86	[14] to 890	
Iron	Filtered	96	55	[4.6] to 2690	72
	<b>Unfiltered</b>	101	86	[4.6] to 10200	
Lead	Filtered	96	16	0.02 to 5.04	26
	Unfiltered	101	35	0.03 to 20.2	
Lithium	Filtered	9	9	5.1 to 8.5	n/a
	Unfiltered	9	9	5 to 9.4	
Magnesium	Filtered	96	94	3600 to 10000	98
	<b>Unfiltered</b>	101	99	3100 to 10000	
Manganese	Filtered	96	70	[0.21] to 116	79
	<b>Unfiltered</b>	101	85	[0.21] to 1080	
Mercury	Filtered	96	6	[0.01] to 0.76	6
	Unfiltered	101	6	$[0.01]$ to 1	

**Table 4.4-1 Frequency of Detected Inorganic Chemicals in Spring Samples Quarterly Sampling from March 1998 through July 2002** 





*Source:* EPA 1989, 08021.

a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$  n/a = Not applicable.



Table 4.4-2<br>Screening of Inorganic Chemicals Detected in Spring Samples **Screening of Inorganic Chemicals Detected in Spring Samples Table 4.4-2** 





**Table 4.4-2 (continued)**  Table 4.4-2 (continued)

*Sources:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or<br>designated uses unless otherwise specified in 20.6.4 designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867; California DHS 2003, 76862.

a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103). a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103).

<sup>b</sup> NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900). b NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $c_{n/a}$  = Not applicable.  $c$   $n/a =$  Not applicable.

 $d(U)$  = The chemical is classified "undetected."  $d(U)$  = The chemical is classified "undetected."

e (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. e (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). f NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

 $9$  na = Not available. g na = Not available.

(U+) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.  $h_{(J+)}$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.

NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103). i NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

j NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900). NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900)

2003 California DHS Action Level. k 2003 California DHS Action Level.

<b>Chemical</b> <b>Retained/Eliminated</b>		Rationale for Retaining/Eliminating as a COPC		
Aluminum	Eliminated	A geochemical evaluation determined that the concentrations are within the naturally-occurring concentration range.		
Antimony	<b>Retained</b>	Detection limit exceeds screening limit.		
Arsenic	Eliminated	A geochemical evaluation determined that the concentrations are within the naturally-occurring concentration range.		
<b>Barium</b>	<b>Retained</b>	Maximum value exceeds screening limit.		
Beryllium	Eliminated	No values above screening limit.		
<b>Boron</b>	<b>Retained</b>	Maximum value exceeds screening limit.		
Cadmium	Eliminated	No values above screening limit.		
Calcium	Eliminated	Essential nutrient.		
Cesium	<b>Retained</b>	No screening value available, retained for further evaluation.		
Chloride	Eliminated	No values above screening limit.		
Chromium	Eliminated	No values above screening limit.		
Cobalt	Eliminated	No values above screening limit.		
Copper	Eliminated	No values above screening limit.		
Cyanide (Total)	<b>Retained</b>	Detection limit exceeds screening limit.		
Fluoride	Eliminated	No values above screening limit.		
Iron	Eliminated	Essential nutrient.		
Lead	Eliminated	A geochemical evaluation determined that the concentrations are within the naturally-occurring concentration range.		
Lithium	Eliminated	No values above screening limit.		
Magnesium	Eliminated	Essential nutrient.		
Manganese	Eliminated	A geochemical evaluation determined that the concentrations are within the naturally-occurring concentration range.		
Mercury	<b>Retained</b>	Maximum value exceeds screening limit.		
Molybdenum	Eliminated	No values above screening limit.		
Nickel	Eliminated	No values above screening limit.		
Nitrate	Eliminated	No values above screening limit.		
Nitrate-Nitrite (as N)	<b>Retained</b>	Maximum value exceeds screening limit.		
Perchlorate	<b>Retained</b>	Maximum value exceeds screening limit.		
Potassium	Eliminated	Essential nutrient.		
Rubidium	<b>Retained</b>	No screening value available, retained for further evaluation.		
Selenium	Eliminated	A geochemical evaluation determined that the concentrations are within the naturally-occurring concentration range.		
Silver	Eliminated	No values above screening limit.		
Sodium	Eliminated	Essential nutrient.		
Strontium	Eliminated	No values above screening limit.		
Sulfate	Eliminated	No values above screening limit.		
Thallium	<b>Retained</b>	Maximum value exceeds screening limit.		
Uranium	<b>Retained</b>	Maximum value exceeds screening limit.		
Vanadium	Eliminated	No values above screening limit.		
Zinc	Eliminated	No values above screening limit.		

**Table 4.4-3 Retained and Eliminated Inorganic Chemicals in Spring Samples** 



**16-02650 Martin Spring Barium Unfiltered Concentrations**

**Figure 4.4-1a. Concentration versus time for barium at Martin Spring. The screening level for barium is 1000 µg/L (off-scale). Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the interim measure at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**16-02651 SWSC Spring Barium Unfiltered Concentrations**

**Figure 4.4-1b. Concentration versus time for barium at SWSC Spring. The screening level for barium is 1000 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the interim measure at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8. Note that SWSC Spring stopped flowing in December 2001.** 



**16-02652 Burning Ground Spring Barium Unfiltered Concentrations**

**Figure 4.4-1c. Concentration versus time for barium at Burning Ground Spring. The screening level for barium is 1000 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the interim measure at the 260 outfall source area (green;**  September 2000). Where temporal trends are significant, p-values and r<sup>2</sup> values are **shown. Points in red represents samples collected during high-flow periods as defined in section 4.4.2.1.8.** 

For Martin Spring, calcium and chloride (Figures I3-1 and I3-2) both show significant increases in concentration over time, whereas neither of the contaminants shows significant trends (Figures 4.4-1a, I3-4, I3-5). The trends for calcium and chloride could be a drought effect resulting in higher concentration of these elements. During high-flow periods, most of the constituents show lower concentrations (presumably a result of dilution) except for iron (filtered and unfiltered; Figures I3-3, I3-6), which has higher concentrations during these periods (presumably as a result of flushing of the hydrogeologic system). No significant temporal trends exist for SWSC Spring. Only filtered iron (i.e., dissolved iron and particles less than 0.45 microns in size) shows an increase during high-flow events (Figure I3-19). The rest of the constituents show no large response in this regard. For Burning Ground Spring, calcium concentrations increase over time (Figure I3-27), whereas iron (filtered and unfiltered), barium, and nitrate decrease over time (Figures I3-29, I3-30, 4.4-1c, I3-32). The decrease in contaminant concentrations could be due to the effect of the implemented IM or to an increased proportion of base flow concentrated in well-flushed (i.e., less contaminated) portions of the vadose zone (see section 5). With the exception of iron (Figures I3-29, I3-32), high-flow periods did not seem to result in major differences in chemical concentrations. No distinct seasonality can be seen in the data, except for some values associated with the winter of 2001, which followed a relatively wet fall and abundant January precipitation (see Appendix B). The lack of seasonal effects is not surprising given the prolonged drought experienced at the site. During the drought, the amplitude of seasonal flow variations has decreased (see sections 4.4.2.1.8 and 4.4.2.1.9). Because concentration trends are influenced by spring discharge rates, plots of mass (concentration multiplied by discharge) are presented in section 4.5 to account for variation in discharge rates.

Figures 4.4-1a–c, I3-1 through I3-6, I3-14 through I3-19, and I3-27 through I3-32 also demonstrate the very high variability that exists for a number of inorganic chemicals, particularly metals such as iron where data can vary over three orders of magnitude. Nitrate concentrations are also highly variable. As seen in Table 4.4-1, no large systematic differences exist for filtered versus unfiltered inorganic chemical with the exception of some metals such as iron in which unfiltered samples typically have higher concentrations. The time series plots shown in Figures 4.4-1a–c, I3-1 through I3-6, I3-14 through I3-19, and I3-27 through I3-32 also demonstrate that, except where significant temporal trends exist, inorganic chemical concentrations from samples collected during the Phase III RFI are similar to those found during the Phase II RFI (pre-1998). One other feature of the data worth noting is that there are no obvious lasting offsets in baseline levels for contaminants associated with either the fire or the IM. Any differences that do occur post-fire or post-IM appear to be part of long-term trends predating the fire or the IM.

For many inorganic chemicals, concentrations are found to be higher at Martin Spring in Martin Spring Canyon relative to Burning Ground and SWSC Springs in Cañon de Valle. Figures 4.4-2a and 4.4-2b show binary concentration plots for selected analytes. Box plots for several metals are shown in Figures 4.4-3a–f. These analyses demonstrate the chemical differences or similarities between the three springs. A quick, robust, graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot (EPA 1992, 73789). These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50% of the data points so that the top of the box represents the 75th percentile and the bottom of the box represents the 25th percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to either 1.5 times the interquartile distance (IQD) (i.e., range between 25th and 75th percentiles) or to the maximum point, whichever is larger. The lower whisker extends either 1.5 times the IQD or to the minimum point, whichever is smaller. Values outside the whiskers are shown as  $\circ$  or  $*$ , representing distinct points for either outliers (above 1.5 times the IQD) or extreme values (above 3 times the IQD). Martin Spring has higher nitrate + nitrite, chloride, and calcium concentrations and lower barium concentrations than either Burning Ground of SWSC Springs. Another metal substantially more concentrated at Martin Spring is boron.



**Figure 4.4-2a. Nitrate + nitrite versus barium concentration plot for springs ("Outliers" have been removed)** 







**Figure 4.4-3a. Box plot comparison of calcium at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-3b. Box plot comparison of chloride at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-3c. Box plot comparison of unfiltered iron at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-3d. Box plot comparison of filtered iron at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-3e. Box plot comparison of barium at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-3f. Box plot comparison of nitrate + nitrite (as N) at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers. Note that extreme outliers mentioned in the text were not included in this analysis.** 

As noted in the Phase II RFI report (LANL 1998; 59891), the concentrations of many metals at the TA-16 springs are higher than in background springs (i.e., Apache Spring, Cañon de Valle Spring, Water Canyon Gallery, Pike Spring, and Seven Springs) upgradient from Laboratory property, indicating many of these metals are anthropogenic in origin. Such comparisons, however, must be viewed with caution since the background springs are from the Sierra de los Valles mountain front, whereas the TA-16 springs are located on the Pajarito Plateau in a different geologic setting.

## **4.4.2.1.2 Springs—Evaluation of Organic Chemicals**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. Table G-2.20 (located in Appendix G-2) provides a summary of all detected organic chemicals for the springs. Frequency of detected organic chemicals, screening results, and retained and eliminated tables for organic chemicals in the springs are presented in Tables 4.4-4, 4.4-5, and 4.4-6, respectively. COPCs retained include dinitrobenzene[1,3-], nitrobenzene, RDX, and TNT. Only RDX and TNT are retained as COPCs based on percentage of detected values. Dinitrobenzene[1,3-] and nitrobenzene had detection limits that exceed the screening limits.

No significant trends in concentration for RDX or the RDX/HMX ratio are found for any of the three springs (Figures 4.4-4a–f). At Martin Spring, the lowest RDX concentrations are found during high-flow periods. The opposite is true at SWSC Spring, whereas no clear difference is found at Burning Ground Spring. There are also no obvious patterns related to seasonality. RDX concentrations vary over 1 to 2 orders of magnitude. The multiple, long time-series shown in Figures 4.4-4a–f demonstrate that concentrations observed during Phase III of the RFI investigation did not differ greatly from those observed during Phase II. No long-term fire- or IM-related baseline shifts are noted.

Figures 4.4-5 and 4.4-6a–c compare RDX and HMX concentrations at the three springs. Martin Spring has the highest RDX and HMX concentrations, but the lowest RDX/HMX ratio. This indicates that Martin Spring may be influenced by a different contaminant source with a greater HMX component or is receiving a greater proportion of recent HE contamination. HMX has been used in HE formulations more commonly than RDX in recent years.

The springs were also analyzed for radionuclides including isotopic plutonium and isotopic strontium following the Cerro Grande fire. These constituents were not detected in spring water. Results of tritium analyses (both pre- and post-fire) are documented in section 4.4.2.1.3.

## **4.4.2.1.3 Springs—Evaluation of Tritium**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of the detected tritium in springs samples collected is provided in Table G-2.21 (located in Appendix G-2). The frequency of detected tritium (Table 4.4-7), the screening results (Table 4.4-8), and the retained and eliminated analysis (Table 4.4-9) are presented in this section. The results show that tritium was not present above either the EPA MCL or the NMWQCC regulations numeric standard.

## **4.4.2.1.4 90s Line Pond—Evaluation of Inorganic Chemicals**

A summary of all samples submitted for laboratory analyses is provided in Appendix G-1. A summary of all detected inorganic chemicals in water is provided in Table G-2.22 (Appendix G-2). Frequency of detected inorganic chemicals, screening results, and retained and eliminated tables for inorganic chemicals in 90s Line Pond are shown in Tables 4.4-10, 4.4-11, and 4.4-12, respectively.

<b>Chemical</b>	<b>Field</b> Preparation	<b>Number</b> οf <b>Analyses</b>	<b>Number</b> of Detects	Concentration Range (µg/L)	<b>Percent Detected</b> for 20 Samples or Greater <sup>a</sup>	
Acetone	Filtered	3	3	21 to 28	31	
	Unfiltered	49	13	$[1.6]^{b}$ to 78		
Amino-2,6-dinitrotoluene[4-]	Filtered	6	3	$[0.25]$ to $[5]$	55	
	Unfiltered	76	42	$[0.1]$ to $[10]$		
Amino-4,6-dinitrotoluene[2-]	Filtered	$6\phantom{1}6$	3	$[0.25]$ to $[5]$	51	
	Unfiltered	76	39	$[0.1]$ to $[20]$		
Amino-x,6-dinitrotoluene[x-]	Filtered	3	$\overline{2}$	[0.39] to 6.6	68	
	Unfiltered	22	15	[0.39] to 7.8		
Butanone <sup>[2-]</sup>	Unfiltered	50	6	$[1.17]$ to $[20]$	11	
Dichlorobenzene[1,4-]	Unfiltered	62	$\mathbf{1}$	$[0.17]$ to $[20]$	$\mathbf{1}$	
Dinitrobenzene[1,3-]	Unfiltered	98	5	[0.021] to [20]	5	
Dinitrotoluene[2,4-]	Filtered	11	$\mathbf{1}$	$[0.034]$ to $[10]$	$\overline{2}$	
	Unfiltered	109	$\mathbf{1}$	[0.034] to [20]		
Dinitrotoluene[2,6-]	Unfiltered	109	$\mathbf 1$	[0.042] to [20]	1	
<b>DNX</b>	Unfiltered	13	4	0.091 to [0.5]	n/a <sup>c</sup>	
<b>HMX</b>	Filtered	9	7	1.7 to [20]	80	
	Unfiltered	98	79	0.89 to 32		
<b>MNX</b>	Unfiltered	13	5	$0.1$ to $[0.5]$	n/a	
Nitrobenzene	Unfiltered	109	3	[0.052] to [200]	3	
<b>RDX</b>	Filtered	9	9	12 to 160	98	
	Unfiltered	98	96	[0.87] to 330		
Tetrachloroethene	Unfiltered	50	23	$[0.2]$ to $[5]$	43	
<b>TNX</b>	Unfiltered	13	4	$[0.059]$ to $[0.5]$	n/a	
Toluene	Unfiltered	50	$\mathbf 1$	$[0.16]$ to $[5]$	$\overline{2}$	
Trichloro-1,2,2- trifluoroethane[1,1,2-]	Unfiltered	40	1	$[0.2]$ to $[5]$	$\overline{2}$	
Trichloroethane[1,1,1-]	Unfiltered	50	1	$[0.25]$ to $[5]$	$\overline{2}$	
Trichloroethene	Unfiltered	50	32	$0.56$ to $[5]$	60	
Trichlorofluoromethane	Unfiltered	50	$\mathbf 1$	$[0.46]$ to $[5]$	$\overline{2}$	
	Filtered	9	$6\phantom{1}$	$[0.2]$ to $[5.2]$	47	
Trinitrobenzene[1,3,5-]	Unfiltered	98	44	$[0.1]$ to $[21]$		
Trinitrotoluene[2,4,6-]	Filtered	9	$\mathbf{1}$	$[0.048]$ to $[5]$	5	
	Unfiltered	97	4	[0.048] to [20]		

**Table 4.4-4 Frequency of Detected Organic Chemicals in Spring Samples from Quarterly Sampling from March 1998 through July 2002** 

*Source:* EPA 1989, 08021.

a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.

 $c$  n/a = Not applicable.



Screening of Organic Chemicals in Spring Samples **Screening of Organic Chemicals in Spring Samples**  Table 4.4-5 **Table 4.4-5** 



Table 4.4-5 (continued)

Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or  $\frac{1}{2}$ ಕ<br>⊇ u<br>Ru Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards appl<br>designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a na = Not available.  $a$  na = Not available.

 $b(D)$  = The chemical is classified "not detected."  $(b(U)$  = The chemical is classified "not detected."

 $c$  (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. c (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

d n/a = Not applicable.  $d$   $n/a$  = Not applicable.

e (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias. e (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias.

f (J+) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias. (J+) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential positive bias.

g (UJ) = The chemical is classified "not detected" with an expectation that the reported result is more uncertain than usual. 9 (UJ) = The chemical is classified "not detected" with an expectation that the reported result is more uncertain than usual

h NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). h NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).
Analyte	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Acetone	Eliminated	No values above screening limit.
Amino-2.6- dinitrotoluene[4-]	Eliminated	No values above screening limit.
Amino-4,6- dinitrotoluene[2-]	Eliminated	No values above screening limit.
Amino-x,6- dinitrotoluene[x-]	Eliminated	No values above screening limit.
Butanone <sup>[2-]</sup>	Eliminated	No values above screening limit.
Dichlorobenzene[1,4-]	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Dinitrobenzene[1,3-]	<b>Retained</b>	Detection limit exceeds screening limit.
Dinitrotoluene[2,4-]	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Dinitrotoluene[2,6-]	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
<b>DNX</b>	Eliminated	No values above screening limit.
<b>HMX</b>	Eliminated	No values above screening limit.
<b>MNX</b>	Eliminated	No values above screening limit.
Nitrobenzene	<b>Retained</b>	Less than 5% of analyses result in a detection but the detection limit exceeds the screening limit.
<b>RDX</b>	<b>Retained</b>	Detected value exceeds screening limit.
Tetrachloroethene	Eliminated	No values above screening limit.
<b>TNX</b>	Eliminated	No values above screening limit.
Toluene	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Trichloro-1,2,2- trifluoroethane[1,1,2-]	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Trichloroethane[1,1,1-]	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Trichloroethene	Eliminated	No values above screening limit.
Trichlorofluoromethane	Eliminated	More than 20 analyses were performed and the number of detected values comprise less than 5% of the total number of analyses.
Trinitrobenzene[1,3,5-]	Eliminated	No values above screening limit.
Trinitrotoluene[2,4,6-]	<b>Retained</b>	Detected value exceeds screening limit.

**Table 4.4-6 Retained and Eliminated Organic Chemicals in Spring Samples** 



**16-02650 Martin Spring RDX Unfiltered Concentrations** 

**Figure 4.4-4a. Concentration versus time for RDX at Martin Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**16-02650 Martin Spring RDX/HMX Ratio Unfiltered** 

**Figure 4.4-4b. Concentration versus time for RDX/HMX at Martin Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**16-02651 SWSC Spring RDX Unfiltered Concentrations**

**Figure 4.4-4c. Concentration versus time for RDX at SWSC Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Open symbols are non-detects. Points in red (open or filled) represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**16-02651 SWSC Spring RDX/HMX Ratio Unfiltered** 

**Figure 4.4-4d. Concentration versus time for RDX/HMX at SWSC Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**16-02652 Burning Ground Spring RDX Unfiltered Concentrations**

**Figure 4.4-4e. Concentration versus time for RDX at Burning Ground Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



#### **16-02652 Burning Ground Spring RDX/HMX Ratio Unfiltered**

**Figure 4.4-4f. Concentration versus time RDX/HMX at Burning Ground Spring. The EPA Region 6 PRG for RDX in drinking water is 0.61 µg/L. Vertical lines mark dates of the Cerro Grande fire (orange; May 2000) and the IM at the 260 outfall source area (green; September 2000). Points in red represent samples collected during high-flow periods as defined in section 4.4.2.1.8.** 



**Figure 4.4-5. RDX concentration versus HMX concentration in springs** 



**Figure 4.4-6a. Box plot comparison of RDX at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-6b. Box plot comparison of HMX at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 



**Figure 4.4-6c. Box plot comparison of RDX/HMX at Martin Spring, SWSC Spring, and Burning Ground Spring. Means are indicated by solid squares. The y-axis represents concentration in µg/L. Center horizontal line is the median, lower and upper horizontal lines are the first and third quartiles respectively. Vertical lines extend to lowest value within the lower limit and the upper value within the upper limits. Stars represent outliers.** 

# **Table 4.4-7 Frequency of Detected Tritium in Spring Samples March 1998 to July 2002**



*Source:* EPA 1989, 08021.

a The percent detection value is calculated based on all analyses taken for a chemical. Resulting values might therefore appear less than expected due to the inclusion of undetects not reported by this table.

b Values in brackets are below detection limits, although some chemicals may be detected at values within this range.



### **Table 4.4-8 Screening of Tritium in Spring Samples**

*Sources:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $<sup>b</sup>$  n/a = Not applicable.</sup>

 $c$  (U) = The chemical is classified "undetected."

#### **Table 4.4-9 Retained and Eliminated Tritium in Spring Samples**



Chemical	<b>Field Preparation</b>	Number of <b>Analyses</b>	Number of <b>Detects</b>	Concentration Range (µg/L)
Aluminum	Filtered	6	6	418 to 4490
	Unfiltered	8	8	4330 to 390000
	Filtered	6	$\overline{c}$	2.8 to [20]*
Antimony	Unfiltered	8	$\overline{3}$	0.923 to [20]
Arsenic	Filtered	6	3	$[2]$ to $[4]$
	Unfiltered	$\overline{7}$	$\overline{7}$	3.8 to 80
<b>Barium</b>	Filtered	6	$6\phantom{a}$	1260 to 6700
	Unfiltered	8	8	3170 to 67000
Beryllium	Filtered	6	$\mathbf 0$	$[0.06 \text{ to } 4]$
	Unfiltered	8	$\overline{7}$	[0.28] to 24
Boron	Filtered	5	5	16.4 to 43.7
	Unfiltered	$\overline{7}$	6	16.8 to [500]
Cadmium	Filtered	6	$\mathbf{1}$	$0.109$ to $[5]$
	Unfiltered	8	3	$[0.2]$ to 5.9
Calcium	Filtered	6	6	4180 to 16000
	Unfiltered	8	8	11500 to 67000
Chloride	Unfiltered	$\overline{7}$	$\overline{7}$	2500 to 22000
Chromium	Filtered	$6\phantom{a}$	$\overline{2}$	$[0.5]$ to $[10]$
	Unfiltered	8	$\overline{7}$	2.6 to [180]
Cobalt	Filtered	$6\phantom{1}6$	4	1 to [20]
	Unfiltered	8	8	0.61 to 72
Copper	Filtered	6	$\overline{\mathbf{4}}$	1.7 to [20]
	Unfiltered	8	7	4.7 to [240]
Cyanide (Total)	Unfiltered	1	0	$[10 \text{ to } 10]$
Fluoride	Unfiltered	$\overline{7}$	7	150 to 391
<b>Iron</b>	Filtered	6	6	380 to 2260
	Unfiltered	8	8	4500 to 310000
Lead	Filtered	6	3	0.733 to 5.3
	Unfiltered	8	8	4.8 to 520
Lithium	Unfiltered	1	$\mathbf{1}$	234 to 234
Magnesium	Filtered	6	5	1220 to [3800]
	Unfiltered	8	7	3690 to [47000]
Manganese	Filtered	6	6	14.5 to 520
	Unfiltered	8	8	81.2 to 3800
Mercury	Filtered	6	$\mathbf 1$	$[0.02]$ to $[0.2]$
	Unfiltered	8	5	$[0.02]$ to 1

**Table 4.4-10 Frequency of Detected Inorganic Chemicals in 90s Line Pond Samples March 1998 through July 2002** 



## **Table 4.4-10 (continued)**

*Source:* EPA 1989, 08021.

\*Values in brackets are below detection limits, although some chemicals may be detected at values within this range.





# Screening of Inorganic Chemicals in 90s Line Pond Samples **Screening of Inorganic Chemicals in 90s Line Pond Samples Table 4.4-11 Table 4.4-11**

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Table 4.4-11 (continued)

*Sources:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards ap<br>designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Pa designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867. Sources:

a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103). a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103).

<sup>b</sup> NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900). b NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $c_{n/a}$  = Not applicable.  $c$  n/a = Not applicable.

 $d(U)$  = The chemical is classified "undetected."  $d(u)$  = The chemical is classified "undetected."

e NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). e NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). (U) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. f (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.  $9$  na = Not available. g na = Not available.

h NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103). h NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

NMVQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900). i NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900).

(UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain than usual. j (UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain than usual.

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<b>Chemical</b>	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Aluminum	<b>Retained</b>	Maximum value exceeds screening limit.
Antimony	<b>Retained</b>	Maximum value exceeds screening limit.
Arsenic	<b>Retained</b>	Maximum value exceeds screening limit.
<b>Barium</b>	<b>Retained</b>	Maximum value exceeds screening limit.
Beryllium	<b>Retained</b>	Maximum value exceeds screening limit.
Boron	Eliminated	No values above screening limit.
Cadmium	<b>Retained</b>	Maximum value exceeds screening limit.
Calcium	Eliminated	Essential nutrient.
Chloride	Eliminated	No values above screening limit.
Chromium	<b>Retained</b>	Maximum value exceeds screening limit.
Cobalt	<b>Retained</b>	Maximum value exceeds screening limit.
Copper	Eliminated	No values above screening limit.
Fluoride	Eliminated	No values above screening limit.
Iron	Eliminated	Essential nutrient.
Lead	<b>Retained</b>	Maximum value exceeds screening limit.
Lithium	Eliminated	No values above screening limit.
Magnesium	Eliminated	Essential nutrient.
Manganese	<b>Retained</b>	Maximum value exceeds screening limit.
Mercury	<b>Retained</b>	Maximum value exceeds screening limit.
Molybdenum	Eliminated	No values above screening limit.
Nickel	Eliminated	No values above screening limit.
Nitrate-Nitrite as N	Eliminated	No values above screening limit.
Potassium	Eliminated	<b>Essential nutrient.</b>
Selenium	<b>Retained</b>	Detection limit exceeds screening limit.
Silver	Eliminated	No values above screening limit.
Sodium	Eliminated	<b>Essential nutrient.</b>
Strontium	Eliminated	No values above screening limit.
Sulfate	Eliminated	No values above screening limit.
Thallium	<b>Retained</b>	Maximum value exceeds screening limit.
Uranium	<b>Retained</b>	Maximum value exceeds screening limit.
Vanadium	<b>Retained</b>	Maximum value exceeds screening limit.
Zinc	Eliminated	No values above screening limit.

**Table 4.4-12 Retained and Eliminated Inorganic Chemicals in 90s Line Pond Samples** 

The following inorganic chemicals failed screening because of a detected value above the screening standard; aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, selenium, thallium, uranium, and vanadium. Of these, aluminum, barium, lead, and manganese were most frequently above screening limits. Unfiltered samples typically have higher concentrations than filtered samples (Table 4.4.10). In general, many of the inorganic chemicals noted here are present at higher concentrations than in the springs (e.g., barium), particularly in unfiltered samples.

#### **4.4.2.1.5 90s Line Pond—Evaluation of Organic Chemicals**

A summary of all samples submitted for laboratory analyses is provided in Appendix G-1. A summary of all detected organic chemicals is provided in Table G-2.23 (Appendix G-2). Frequency of detected organic chemicals, screening results, and retained and eliminated tables for organic chemicals in the 90s Line Pond are shown in Tables 4.4-13, 4.4-14, and 4.4-15, respectively. The only organic chemical for which a screening value is available and for which a detected value exceeds that limit is RDX. RDX concentrations at 90s Line Pond are somewhat lower than in the springs.

#### **4.4.2.1.6 90s Line Pond—Tritium**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of the detected tritium in 90s Line Pond samples collected is provided in Table G-2.24 (Appendix G-2). The frequency of detected tritium (Table 4.4-16), the screening results (Table 4.4-17), and the retained and eliminated analysis (Table 4.4-18) are presented in this section. The results show that tritium was not present above either the EPA MCL or the NMWQCC regulations numeric standard.

#### **Table 4.4-13 Frequency of Detected Organic Chemicals in 90s Line Pond Samples March 1998 through July 2002**



*Source:* (EPA 1989, 08021.

\*Values in brackets are below detection limits, although some chemicals may be detected at values within this range.



Screening of Organic Chemical in 90s Line Pond Samples **Screening of Organic Chemical in 90s Line Pond Samples**  Table 4.4-14 **Table 4.4-14** 

Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or<br>designated uses unless otherwise specified in 20.6.4 Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or

a (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias. a (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias. designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

 $b_{n}$  na = Not available.  $b_{\text{na}}$  = Not available.

 $C(U)$  = The chemical is classified "not detected."  $c$  (U) = The chemical is classified "not detected."

<sup>d</sup> (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.<br><sup>e</sup> NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). d (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

e NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

 $f_{\text{I}}$   $n/a$  = Not applicable.  $f_1$   $n/a$  = Not applicable.





#### **Table 4.4-16 Frequency of Detected Tritium in 90s Line Pond Samples March 1998 to July 2002**



*Source:* EPA 1989, 08021.





*Sources:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $<sup>b</sup>$  n/a = Not applicable.</sup>

 $c$  (U) = The chemical is classified "undetected."

# **Table 4.4-18**

#### **Retained and Eliminated Results Tritium in 90s Line Pond Samples**



## **4.4.2.1.7 Stable Isotopes (**δ18**O,** δ**D, and** δ15**N) and Tritium**

Stable isotope data ( $\delta^{18}O$  and  $\delta D$ ) were collected to better understand hydrologic behavior of the TA-16 spring systems. Details of the assessment are included in section 5. The variations in the  $\delta^{18}O$  of spring water reflect variations in stable isotope content of rain and snowmelt, as well as mixing in the vadose zone. The  $\delta^{18}$ O data are shown in Figure 4.4-7, and the data are available in the screening data provided in Appendix H. The δD data show similar behavior and are not presented in this document. The data do not show any substantial evaporative effects indicating relatively rapid movement of water though the near-surface evaporative zone. Values for Burning Ground Spring and SWSC Spring are similar, indicating they probably share similar recharge pathways and residence times. However, the  $\delta^{18}O$  values of Martin Spring are quite distinctive compared with Burning Ground Spring and SWSC Spring. The Martin Spring values are predominantly larger than the values in the other springs and thus indicate Martin Spring has a different set of recharge pathways and residence times. The larger values also indicate Martin Spring might be recharged from lower elevations than the other springs or that it has a larger proportion of lower elevation recharge.

The nitrogen stable isotope data ( $\delta^{15}N$ ) were collected as a possible way of examining impacts from anthropogenic nitrate (i.e., nitrate derived from HE and barium nitrate) in the spring water. The nitrogen stable isotope data ( $\delta^{15}N$ ) and associated nitrate concentrations for the springs are shown in Table 4.4-19. The average  $\delta^{15}N$  values in the springs are nearly identical, 2.93 permil (‰) at Burning Ground Spring, 3.34 permil at Martin Spring, and 3.32 permil at SWSC Spring. There is a large temporal variation in each spring, and the mean values have large standard deviations ranging from 1.24 to 2.33. The results do not show any significant differences compared with expected values for natural nitrates from forested environments (Clark and Fritz 1997, 59168). Thus, the nitrogen isotope results are uninformative in terms of assessing the impact of anthropogenic nitrogen on TA-16 spring water.

Tritium concentrations in spring water over time are shown in Figure 4.4-8. These values are similar to TA-16 values discussed previously in the Phase I RFI (LANL 1996, 55077). The values reflect variations in tritium concentrations in precipitation and any vadose zone mixing between water of different ages. The relatively high levels of tritium indicate the spring water has relatively short residence time of less than a few decades and probably much less. This is because the tritium present at LANL has not decayed away and "old water" (pre-event water with a long residence time) has tritium values approaching zero Tritium Units. The tritium results support the interpretations from  $\delta^{18}O$  results in that the similar values for Burning Ground Spring and SWSC Spring indicate similar recharge pathways and residence times. In addition, Martin Spring often has higher tritium concentrations indicating a different distribution of residence times than Burning Ground Spring or SWSC Spring, which is again consistent with the  $\delta^{18}$ O results.

### **4.4.2.1.8 Spring Dynamics**

The flow records of Shaull et al. (2003, 76042) are used to document flow at the springs as these records represent the most complete and longest time-series available. All three springs were instrumented with an ultrasonic flow logger. The hydrographic record for the three springs is shown in Figures 4.4-9a–c and the data are provided in Appendix H. The precipitation record for TA-16 is provided in Appendix B. The springs were also instrumented to measure parameters such as temperature, pH, and conductivity. These data are also tabulated in Appendix H. All three records show some seasonality in flow, particularly in the first half of the time series. During the drought years of 1998 through 2002 (the years covered by this report), seasonality is more damped out and only distinct high-flow events show up as prominent peaks. From 1998 through 2002, the most prominent of these events was the winter discharge of 2001 (Figures 4.4-9a–c). This event occurred following above-average fall precipitation in 2000 and aboveaverage precipitation for January 2001. The most dramatic trend is the drying up of SWSC Spring in late

2001. Martin Spring and Burning Ground Spring are experiencing flow decreases over time with Martin Spring drying up briefly during the summer of 2003.

The relationship between pre-1998 precipitation events (i.e., during an overall wetter period) and spring discharge is discussed in the Phase II RFI report (LANL 1998, 59891). Relatively rapid connectivity between precipitation water and the springs is indicated. Due to pervasive drought conditions, this type of relationship is not confirmed in the present data set.



**Figure 4.4-7. Stable Isotope (**δ**18O) variations with time in the three TA-16 springs** 

<b>Spring</b>	Location	<b>Collection</b> <b>Date</b>	<b>Chemical Name</b>	Nitrate (NO <sub>3</sub> $\mu$ g/L)	$\delta^{15}$ N permil
Martin	16-02650	9/25/1998	Nitrite (as $NO2$ )	100	4.2
Martin	16-02650	12/15/1998	Nitrate – Nitrite (as $N$ )	4400	3.1
Martin	16-02650	6/23/1999	Nitrite (as $NO2$ )	100	$-0.9$
Martin	16-02650	3/31/2000	Nitrate - Nitrite (as N)	50	1.3
Martin	16-02650	8/25/2000	Nitrate - Nitrite (as N)	4400	1.5
Martin	16-02650	8/28/2000	Nitrate - Nitrite (as N)	3800	3.9
Martin	16-02650	9/22/2000	Nitrate - Nitrite (as N)		5.3
Martin	16-02650	9/29/2000	Nitrate - Nitrite (as N)	5100	5.3
Martin	16-02650	11/20/2000	Nitrate – Nitrite (as $N$ )	3760	6.5
Martin	16-02650	1/10/2001	Nitrate - Nitrite (as N)	4620	5.5
<b>SWSC</b>	16-02651	3/30/1998	Nitrate (as $NO3$ )	900	4.3
<b>SWSC</b>	16-02651	6/23/1998	Nitrate - Nitrite (as N)	980	1.8
<b>SWSC</b>	16-02651	6/24/1999	Nitrite (as $NO2$ )	100	1.4
SWSC	16-02651	3/21/2000	Nitrate - Nitrite (as N)	1100	3.1
<b>SWSC</b>	16-02651	8/25/2000	Nitrate - Nitrite (as N)	960	2.2
<b>SWSC</b>	16-02651	8/29/2000	Nitrate - Nitrite (as N)	1000	3
<b>SWSC</b>	16-02651	9/26/2000	Nitrate - Nitrite (as N)	1300	4.6
<b>SWSC</b>	16-02651	9/28/2000	Nitrate - Nitrite (as N)	1200	4.2
<b>SWSC</b>	16-02651	1/8/2001	Nitrate - Nitrite (as N)	1300	5.1
<b>Burning Ground</b>	16-02652	9/25/1998	Nitrate (as $NO3$ )	970	2.3
<b>Burning Ground</b>	16-02652	12/16/1998	Nitrate (as $NO3$ )	910	2.3
<b>Burning Ground</b>	16-02652	6/24/1999	Nitrate (as $NO3$ )	950	1.3
<b>Burning Ground</b>	16-02652	3/31/2000	Nitrate - Nitrite (as N)	910	0.9
<b>Burning Ground</b>	16-02652	8/25/2000	Nitrate - Nitrite (as N)	1000	1.5
<b>Burning Ground</b>	16-02652	8/29/2000	Nitrate - Nitrite (as N)	1100	1.9
<b>Burning Ground</b>	16-02652	9/25/2000	Nitrate - Nitrite (as N)	1300	5.8
<b>Burning Ground</b>	16-02652	9/29/2000	Nitrate – Nitrite (as $N$ )	1100	4.4
<b>Burning Ground</b>	16-02652	11/20/2000	Nitrate - Nitrite (as N)	718	2.7
<b>Burning Ground</b>	16-02652	1/9/2001	Nitrate - Nitrite (as N)	1000	4.2
<b>Burning Ground</b>	16-02652	1/29/2001	Nitrate - Nitrite (as N)	1300	6.5

**Table 4.4-19 Stable Isotope and Nitrate Concentration Values at the TA-16 Springs** 



**Figure 4.4-8. Tritium variations with time in the three TA-16 springs** 









### **4.4.2.1.9 Spring Recharge and Residence Times**

The issues of where the TA-16 springs are recharged and the residence times of water and contaminants in the flow paths to the springs are both important considerations when questions such as "how long will it take to see a benefit from a remedial action (e.g., source removal or run-on controls)" or "what is the relation between recharge and contaminant concentrations in spring water" are evaluated. As part of the Phase III RFI, specialized studies were conducted to provide more information about recharge and the residence times of water in the spring systems. The results of these studies (described in more detail below) show the spring systems are best described as having a distribution of residence times and flow rates and that these distributions are wide enough that they may have important consequences for remediation and monitoring decisions at the springs.

The first study uses stable isotopes of water ( $\delta^{18}$ O and  $\delta$ D) as tracers. These isotopes are naturally occurring components of all water and do not decay. The stable isotopes work well as tracers because certain kinds of water (e.g., a large precipitation event) can have a unique isotopic signature that can be followed from recharge to discharge in the springs. The first approach using the stable isotopes involves measurement of isotopic compositions from individual precipitation events and from the springs. These numbers are used, along with the spring flow measurements, to understand the residence times of water in the spring systems. For this approach, individual precipitation events are examined and old water versus new water ratios using mixing models are calculated. Details of the stable isotope approach and methods and the mixing models are found in the paper "Lateral subsurface flow pathways in a semiarid ponderosa pine hillslope" (Newman et al. 1998, 76883). The isotope data used in the calculations is discussed in Sections 3.3.3.4 and 4.4.2.1.7 and is included in Appendix H. As further explanation of the old/new water concept, if a rain event occurs, an increased flow in a spring is observed. The mixing models are used to determine how much of that flow increase is from old (or pre-event) water that is being "pushed" out by the current rain or how much of the flow increase is new water (directly from the rain event itself). In many hydrologic systems, flow increases are dominated by old water; in others, new water can be important. Percent new water results for the mixing model calculations for some example precipitation events in 1999 are shown in Table 4.4-20. The results show a wide range of values indicating the amount of new versus old water can vary substantially. This variation is largely a function of the size and duration of the precipitation event, the flow rate along a given flow path, and the amount of water stored in the unsaturated and saturated zones. The fact that some events show substantial new water inputs is important. New water shows that some of the recharge occurs rapidly (within 24 hours of the precipitation event) indicating fast preferential flow though the TA-16 mesa. The fact that both new and old water inputs are observed indicates there are probably at least two classes of flow paths for recharge: a group of rapid flow, relatively short flow paths; and another group that represents slower flow and longer flow paths. This idea of two main groups of flow paths is also supported by spectral analysis of spring flow, which is described later in this section. In addition, the two types of flow response support the hydrograph analysis described in the Phase II RFI report (LANL 1998, 59891) that shows both long- and short-term responses of spring flow to precipitation events.

<b>Date</b>	<b>Burning Ground Spring</b> (%)	<b>Martin Spring</b> (%)	<b>SWSC Spring</b> (%)
4/30/99	33	85	48
5/3/99			
06/16/99			
06/17/99	19	61	32
07/14/99			

**Table 4.4-20 Percent New Water from Example Precipitation Events in 1999** 

The stable isotope data from the springs can also be used to estimate the elevation of recharge. This kind of analysis provides an indication of the length of the flow paths from the recharge areas to the springs. The explanation of the approach and details of the calculation are provided in Appendix J. The results indicate the maximum recharge elevation for the springs is about 7800 ft, which is on the scarp of the Pajarito fault. This area is less than 1.5 mi away from the springs, indicating the recharge zone for base flow in the TA-16 springs is relatively close. The elevation calculations also indicate some recharge occurs on the TA-16 mesa itself, consistent with the new water contribution to flow described earlier. An additional point is that isotopic values from Martin Spring are consistently larger (less negative) than either SWSC Spring or Burning Ground Spring (see section 4.4.2.1.7), indicating the recharge zones for Martin Spring occurs at lower elevations than for the other springs, or that Martin Spring has a larger proportion of lower elevation recharge. One uncertainty with this interpretation is that Martin Spring may be impacted by evaporated pond water from the former disposal lagoons at V-Site and possibly the 90s Line Pond, thus biasing the elevation calculation.

The Phase II RFI (LANL 1998, 59891) examined spring hydrologic issues using analysis of spring flow time-series and the singular spectrum approach (see Appendix J). This approach tries to decompose the "noisy" time-series of spring flow (see Appendix J) into physically meaningful spectra in order to understand the time scales that control variability in spring discharge. The results of the spring flow analyses show there are two main flow modes in the spring. These modes support the two main classes of flow paths described in the old/new water discussion above. The first is a longer, base-flow type mode that has characteristic behaviors that reflect "climatic" signals such as annual and seasonal variations. The second is a noise-like rapid recharge mode driven by individual rain or snowmelt events. This mode is consistent with the fact that rapid, new water contributions to the springs are observed.

One final comment that relates to the flow behavior, which also impacts variations in contaminant concentrations in the springs, is that the effects of the recent multi-year drought are quite pronounced. The spring flow time-series show an overall decrease in flow as noted in section 4.4.2.1.8. The spectrum analysis (Appendix J) also shows a decrease in the duration of springtime recharge along the slow "base flow" flow paths. In addition, decreased variability in the stable isotope data during the drought with a notable lack of the normal seasonality that these types of data usually show is observed (Figure 4.4-7).

### **4.4.2.2 Intermediate-Depth Perched Aquifer Characterization**

As part of the Phase II RFI subsurface investigation (LANL 1998, 59891), five wells were drilled to depths between 91 to 207 ft to characterize the intermediate-depth perched aquifer and to define the nature and extent of contamination (Figure 4.4-10). The wells include Well 16-02665 located near Martin Spring Canyon, Well 16-02667 within SWSC Cut, Well 16-02668 near Building 16-300, Well 16-02669 located east of the 90s Line Pond, and Well 16-02712 (now plugged and abandoned) downstream of the TA-16-260 former settling pond. The initial results of the drilling are reported in the Phase II RFI report (LANL 1998, 59891). This section provides an updated stratigraphy, an assessment of the intermediatedepth perched aquifer behavior based on chloride and stable isotope tracers, results of hydraulic testing of core, and groundwater chemistry data from Well 16-02665 (Martin Spring Canyon) from samples collected after completion of the Phase II RFI. Inorganic and organic chemicals in water are reported for a subsurface flow event that occurred in April 1998 at Well 16-02712. This event demonstrates the ephemeral nature of the intermediate-depth perched aquifer within the mesa vadose zone. Prior to drilling, little was known about the stratigraphy, hydrologic properties, vadose zone fluxes, or contaminant distributions in this part of TA-16. Thus, the objective of this study was to collect information that would aid in understanding the flow and transport conditions within the mesa and, where possible, determine contaminant nature and extent (i.e., the types and concentrations of contaminants present and their distributions). The vadose zone at TA-16 is approximately 748 ft thick (Broxton et al. 2002, 72640); however, this study did not investigate the entire thickness of the vadose zone. This study is one of the first hydrogeologic and contaminant characterization efforts on the western part of the Pajarito Plateau.



**Figure 4.4-10. Location map for intermediate-depth perched aquifer wells**

## **4.4.2.2.1 Core Analysis**

Moisture-protected core subsamples were collected for hydrologic property characterization in wells during drilling and for pore-water chloride and pore-water stable isotope analyses in Wells 16-02665, 16-02669, and 16-02667. More details on the drilling method are provided in the Phase II RFI report (LANL 1998, 59891). Analyses of hydrologic properties were conducted by Daniel B. Stephens & Assoc. (D.B. Stephens & Associates, Inc. 1999, 76886) and included gravimetric water content, bulk density, saturated hydraulic conductivity, characteristic curve information, and calculated porosity.

Pore-water chloride and pore-water stable isotope samples were collected approximately every 3 m. To preserve in situ water content, samples are placed in glass septum jars for chloride analyses and ProTecore bags for stable isotope analyses. Pore-water chloride and stable isotope values are determined using methods described in the paper "Tracer-based studies of soil water movement in semiarid forests of New Mexico" (Newman et al. 1997, 76885). Gravimetric water content analyses were performed prior to conducting the chloride leaching analyses (Gardner 1986, 76888). Chloride concentrations were measured using ion chromatography with an analytical precision of +/- 5%. The chloride mass balance approach (Newman et al. 1997, 76885) was used to calculate vadose zone residence times according to:

$$
R = Cl_{\text{cum}} / (Cl_p \times P)
$$

Where R is the vadose zone residence time (yr),  $Cl_{cum}$  is the cumulative chloride content from the ground surface to the depth of interest  $(g/m^2)$ , Cl<sub>p</sub> is the average annual chloride concentration in precipitation (g/m<sup>3</sup>), and P is the average annual precipitation rate (m/yr). For this study, values of 0.29 g/m<sup>3</sup> for Cl<sub>p</sub> (Anderholm 1994, 76887) and 0.5 m/yr (Bowen 1990, 06899) were used.

Stable isotope analyses were conducted at the New Mexico Technical Institute Stable Isotope Laboratory using the distillation method described in Shurbaji et al. (1995, 76882) and the extraction methods described in the Socki et al. (1992, 64064) and Kendall and Coplen (1985, 64061). Analytical precisions for the  $\delta^{18}$ O and  $\delta$ D analyses were 0.2 and 5 permil, respectively. The isotope values are reported based on the Vienna-Standard Mean Ocean Water standard (Clark and Fritz 1997, 79168).

### **4.4.2.2.2 Intermediate-Depth Well Monitoring**

Wells 16-02665, 16-02667, 16-02668, and 16-02669 were monitored for volumetric water content using a calibrated neutron probe. Monitoring was done quarterly from 1999 through 2000. In addition, Wells 16-02665 and 16-02669 were monitored for groundwater levels. Well 16-02665 groundwater was sampled for stable isotopes and HE when the well contained water. Well 16-02669 has not contained water since the initial sampling (this is likely due to the multi-year drought currently being experienced by the region). Water-level information for these wells is included in Appendix H.

# **4.4.2.2.3 Hydrologic Properties Results**

Hydrologic properties data based on geologic unit are shown in Table 4.4-21. The hydrologic data show a wide range in bulk densities, porosities, and saturated hydraulic conductivities that are related to the degree of welding. Surge beds (unwelded ash flows) have the highest porosities, saturated conductivities, and the lowest bulk densities. Partly welded tuff units have intermediate property values and the densely welded units have the highest bulk densities, lowest porosities, and hydraulic conductivities. The laboratory analyses are essentially measuring matrix conductivities; however, core and outcrop observations in the area indicate that open fractures are common in the welded units. Thus, even though the matrix conductivities are low, the fracture conductivities are likely high (Lewis et al. 2002, 73785).

Unit*	Well	<b>Borehole</b> <b>Sample</b> Depth (m)	<b>Volumetric</b> Water <b>Content</b> $(\theta \mathsf{v} [\%])$	<b>Bulk Density</b> $(\rho b [g/cm^3])$	Porosity (%)	<b>Saturated</b> <b>Hydraulic</b> <b>Conductivity Ks</b> (cm/sec)	Welding
4u	16-02668	3.2	6.7	1.73	35	$1.4x10^{-5}$	partly
4u	16-02668	5.8	3.9	1.97	26	$1.2x10^{-6}$	partly
4u	16-02668	9.4	2.4	1.3	51	$3.8x10^{-3}$	surge
3T	16-02667	21.5	7.8	2.13	20	$1.7x10^{-8}$	densely
3T	16-02669	27.4	7.2	2.17	18	$2.0x10^{-8}$	densely
3T	16-02667	27.1	4.6	2.21	17	$9.8x10^{-9}$	densely
3T	16-02667	30.6	7.2	2.16	18	$2.8x10^{-8}$	densely
3	16-02667	36.7	15.4	1.42	47	$5.0x10^{-4}$	surge
3	16-02667	39.5	5.2	1.71	36	$5.8x10^{-5}$	poorly

**Table 4.4-21 Hydrologic Properties of TA-16 Tuff Samples Collected from Intermediate-Depth Perched Aquifer Wells During Drilling** 

\* See "Geology of the Western Part of Los Alamos National Laboratory (TA-3 to TA-16), Rio Grande Rift, New Mexico" (Lewis et al. 2002, 73785) for a description of stratigraphic units.

## **4.4.2.2.4 Water Content Results**

Example volumetric water content results for the wells are shown in Figures 4.4-11a–d. The complete data set is provided in Appendix H. In general, there was little variation in water content with time (typically less than 2%, except at the shallowest depths). Volumetric water contents range from 3% to 23% and average water contents range from 6% to 10% the four wells. Changes in water content with depth appear to be associated with changes in stratigraphy and/or degree of welding. During drilling, water was encountered at approximately 119 ft in the Well 16-02669 (90s Line Pond 4/15/98) and 73 ft in the Well 16-02665 (Martin Spring Canyon 4/13/98). These zones correspond to an interval of fractured, welded tuff. This corresponds to water level elevations of 7456 ft amsl in Well 16-02669 and 7407 ft amsl in Well 16-02665. After the water level stabilized, the wells were bailed dry. No additional flow was observed in Well 16-02669 (90s Line Pond). Well 16-02665 (Martin Spring Canyon) also remained dry most of the time. However, five separate flow events were observed in Well 16-02665 between 1998 and 2002. These events were in response to snowmelt and high rainfall periods. In these groundwater zones, volumetric water contents were about 18%. The calculated porosities for the welded intervals that contain the wet zones range from 16% to 20%, indicating the groundwater zones were near or at 100% saturation between 1998 and 2002. Based on the intermittent flow, the groundwater-producing depths will hereinafter be referred to as transient saturated zones.

### **4.4.2.2.5 Intermediate-Depth Perched Aquifer—Evaluation of Inorganic Chemicals**

Appendix G-1 summarizes the intermediate-depth perched aquifer samples submitted for laboratory analyses. Table G-2.25 (located in Appendix G-2) presents data for all detected inorganic chemicals in the intermediate-depth perched aquifer samples. Chemical analyses of post-1998 Well 16-02665 flow events are shown in Appendix H. A summary of all analytical results is provided in Appendix G-3. Frequency of detected inorganic chemical, screening results, and retained and eliminated tables for inorganic chemicals in the intermediate-depth perched aquifer samples are shown in Tables 4.4-22, 4.4-23, and 4.4-24, respectively. Inorganic chemicals retained as COPCs include aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, and zinc.



# **90s Line Borehole (16-02669)**







**Figure 4.4-11b. Example volumetric water content profiles for Well 16-02668 (Building 300)** 



SWSC Hole (16-02667)

**Figure 4.4-11c. Example volumetric water content profiles the Well 16-02665 (Martin Spring Canyon)** 



SWSC Hole (16-02667)

**Figure 4.4-11d. Example volumetric water content profiles for Well 16-02667 (SWSC Cut)** 

**Table 4.4-22** 

Frequency of Detected Inorganic Chemicals in Intermediate-Depth Perched Aquifer Samples
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# **Table 4.4-22 (continued)**

*Source:* EPA 1989, 08021.

\*Values in brackets are below detection limits, although some chemicals may be detected at values within this range.


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Table 4.4-23 (continued)

So*urces:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or<br>designated uses unless otherwise specified in 20.6 Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103). a NMWQCC Groundwater Standard for Irrigation Use (20 NMAC 6.2.3103).

<sup>b</sup> NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900). b NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $c_{n/a}$  = Not applicable. c n/a = Not applicable.

d (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. d (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

e (UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain than usual. e (UJ) = The chemical is classified "undetected" with an expectation that the reported result is more uncertain than usual.

f NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). f NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

 $9$  (U) = The chemical is classified "undetected."  $g(\bigcup)$  = The chemical is classified "undetected."

 $h_{\text{na}} = \text{Not available}.$ h na = Not available.

NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103). i NMWQCC Groundwater Other Standards for Domestic Water Supply (20 NMAC 6.2.3103).

NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900) j NMWQCC Surface Water Standard for Wildlife Habitat (20 NMAC 6.4.900).

**Table 4.4-24 Retained and Eliminated Inorganic Chemicals in Intermediate-Depth Perched Aquifer Samples** 

<b>Chemical</b>	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Aluminum	<b>Retained</b>	Maximum value exceeds screening limit.
Antimony	<b>Retained</b>	Maximum value exceeds screening limit.
Arsenic	<b>Retained</b>	Maximum value exceeds screening limit.
Barium	<b>Retained</b>	Maximum value exceeds screening limit.
Beryllium	<b>Retained</b>	Maximum value exceeds screening limit.
<b>Boron</b>	<b>Retained</b>	Maximum value exceeds screening limit.
Cadmium	<b>Retained</b>	Maximum value exceeds screening limit.
Calcium	Eliminated	Essential nutrient.
Chloride	Eliminated	No values above screening limit.
Chromium	<b>Retained</b>	Maximum value exceeds screening limit.
Cobalt	<b>Retained</b>	Maximum value exceeds screening limit.
Copper	<b>Retained</b>	Maximum value exceeds screening limit.
Fluoride	Eliminated	No values above screening limit.
Iron	Eliminated	Essential nutrient.
Lead	<b>Retained</b>	Maximum value exceeds screening limit.
Magnesium	Eliminated	Essential nutrient.
Manganese	<b>Retained</b>	Maximum value exceeds screening limit.
Mercury	Eliminated	No values above screening limit.
<b>Nickel</b>	<b>Retained</b>	Maximum value exceeds screening limit.
<b>Nitrate</b>	Eliminated	No values above screening limit.
Nitrate-Nitrite (as N)	Eliminated	No values above screening limit.
Potassium	Eliminated	Essential nutrient.
Selenium	<b>Retained</b>	Maximum value exceeds screening limit.
Silver	<b>Retained</b>	Maximum value exceeds screening limit.
Sodium	Eliminated	Essential nutrient.
Sulfate	Eliminated	No values above screening limit.
Thallium	<b>Retained</b>	Maximum value exceeds screening limit.
Uranium	Eliminated	No values above screening limit.
Vanadium	Eliminated	No values above screening limit.
Zinc	<b>Retained</b>	Maximum value exceeds screening limit.

#### **4.4.2.2.6 Intermediate-Depth Perched Aquifer—Evaluation of Organic Chemicals**

Appendix G-1 summarizes the intermediate-depth perched aquifer samples submitted for laboratory analyses. Table G-2.26 (located in Appendix G-2) presents data for all detected organic chemicals in the intermediate-depth perched aquifer samples. Chemical analyses of post-1998 Well 16-02665 flow events are shown in Appendix H. A summary of all analytical results is provided in Appendix G-3. Frequency of detected organic chemicals, screening results, and retained and eliminated results for organic chemicals in the intermediate-depth perched aquifer are shown in Tables 4.4-25, 4.4-26, and 4.4-27, respectively. HMX and RDX are the prevalent organic COPCs. There was no clear trend in Well 16-02665 concentrations with time, although the 2000 and 2001 flow events had substantially lower concentrations for all types of HE than had been detected previously. The maximum HE detections were all from Well 16-02712. Samples from this well were collected directly under the area where the largest quantity of HE was historically released at TA-16.





*Source:* EPA 1989, 08021.

\*Values in brackets are below detection limits, although some chemicals may be detected at values within this range.



**Screening of Organic Chemicals in Intermediate-Depth Perched Aquifer Samples**  Screening of Organic Chemicals in Intermediate-Depth Perched Aquifer Samples Table 4.4-26 **Table 4.4-26** 

Sources: 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867. a na = Not available.

 $a$  na = Not available.

 $(b(U)$  = The chemical is classified "not detected."  $b(D)$  = The chemical is classified "not detected."

c (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias. c (J-) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual with a potential negative bias. d NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103). d NMWQCC Groundwater Human Health Standard (20 NMAC 6.2.3103).

e n/a = Not applicable. e n/a = Not applicable.

 $(0)$  = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual. f (J) = The chemical is classified "detected," but the reported concentration value is expected to be more uncertain than usual.

<b>Chemical</b>	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Acetone	Eliminated	No values above screening limit.
Amino-2,6-dinitrotoluene[4-]	Eliminated	No values above screening limit.
Amino-4,6-dinitrotoluene[2-]	Eliminated	No values above screening limit.
Amino-x,6-dinitrotoluene[x-]	Eliminated	No values above screening limit.
Dichloroethane[1,2-]	Eliminated	No values above screening limit.
Dinitrotoluene[2,4-]	Eliminated	No values above screening limit.
Dinitrotoluene[2,6-]	Eliminated	No values above screening limit.
<b>HMX</b>	Eliminated	No values above screening limit.
Methylene Chloride	<b>Retained</b>	Maximum value exceeds screening limit.
<b>RDX</b>	<b>Retained</b>	Maximum value exceeds screening limit.
Tetrachloroethene	Eliminated	No values above screening limit.
Trichloroethene	<b>Retained</b>	Maximum value exceeds screening limit.
Trinitrobenzene[1,3,5-]	Eliminated	No values above screening limit.
Trinitrotoluene[2,4,6-]	<b>Retained</b>	Maximum value exceeds screening limit.

**Table 4.4-27 Retained and Eliminated Organic Chemicals in Intermediate-Depth Perched Aquifer Samples** 

#### **4.4.2.2.7 Intermediate-Depth Perched Aquifer—Evaluation of Tritium**

A summary of samples submitted for laboratory analyses is provided in Appendix G-1. A summary of the detected tritium in intermediate-depth perched aquifer samples collected is provided in Table G-2.27 (located in Appendix G-2). The frequency of detected tritium (Table 4.4-28), the screening results (Table 4.4-29), and the retained and eliminated analysis (Table 4.4-30) are presented in this section. The results show that tritium was not present above either the EPA MCL or the NMWQCC regulations numeric standard.

**Table 4.4-28 Frequency of Detected Tritium in Intermediate-Depth Perched Aquifer Samples** 

<b>Chemical</b>	Field	Number of	Number of	<b>Concentration Range</b>
	<b>Preparation</b>	<b>Analyses</b>	<b>Detects</b>	(DC <sub>i</sub> /L)
Tritium	Unfiltered			72 to 103.36

*Source:* EPA 1989, 08021.

**Table 4.4-29** 

#### **Screening of Tritium Detected in Intermediate-Depth Wells Perched Aquifer Samples**



*Sources:* 20 NMAC 6.2.3103 "Standards for groundwater of 10,000 mg/l TDS concentration or less," Parts A, B, and C; 20 NMAC 6.4.900 "Standards applicable to attainable or designated uses unless otherwise specified in 20.6.4.101 through 20.6.4.899 NMAC," Parts K, L, and M; EPA 2002, 76871; EPA 2003, 76867.

a NMWQCC Surface Water Standard for Livestock Watering (20 NMAC 6.4.900).

 $<sup>b</sup>$  n/a = Not applicable.</sup>

**Table 4.4-30 Retained and Eliminated Tritium in Intermediate-Depth Perched Aquifer Samples** 

Chemical	<b>Retained/Eliminated</b>	Rationale for Retaining/Eliminating as a COPC
Tritium	Eliminated	No values above screening limit.

# **4.4.2.2.8 Chloride Results**

Pore water chloride profiles for the Well 16-02669 (90s Line Pond), Well 16-02665 (Martin Spring Canyon), and Well 16-02667 (SWSC Cut) are shown in Figure 4.4-12. Concentrations range from 17 to 1950 mg/L. Like the water content data, changes in chloride concentrations appear to be associated with changes in stratigraphy and degree of welding. Chloride-based vadose zone residence times are 2240 years for the Well 16-02669, 6080 years for the Well 16-02665, and 1950 years for the Well 16-02667 (residence times are based on cumulative chloride from the surface to the top of the transient saturated zones for the Well 16-02669 and Well 16-02665 and at the bottom of Well 16-02667). These long residence times indicate there has been no recharge at the wells for nearly 2000 years or longer. In addition, it appears the downward flux of water in the vadose zone is relatively constant. Cumulative chloride-cumulative water content plots are relatively linear, which is an indicator of approximately constant downward flux (Newman et al. 1997, 76885) (Figure 4.4-13). One exception to the approximately constant linear trends is for the shallow part of Well 16-02669. This deviation likely results from localized near-surface evapotranspiration effects.

Though the chloride results indicate long vadose zone residence times, these results appear to be contradictory to the presence of HE at depth in Wells 16-02669 and 16-02665. The HE data indicate that some recharge to the transient saturated zones has occurred within the last fifty years. This apparent inconsistency is discussed below.

# **4.4.2.2.9 Stable Isotope Results**

Stable isotope (δ18O) profiles for Wells 16-02669, 16-02665, and 16-02667 are shown in Figures 4.4-14 through 4.4-16 (the δD profiles are similar and are not shown). The profiles show values that are generally below -4 permil δ18O at depths above the transient saturated zones and throughout Well 16-02667. However, the isotope values in the transient saturated zones in Well 16-02669 and Well 16-02665 initially showed large positive δ18O and δD values. These data indicate the waters were strongly evaporated. Values that plot far to the right of the meteoric water line are characteristic of evaporation (Vuataz and Goff 1986, 40083) (Figure 4.4-17). Isotopic values above and below the transient saturated zones show little to minor evaporation with the exception of one sample at 15 m in the 90s Line Pond borehole. It is unclear whether this result was caused by a stable isotope sample preservation problem (chloride concentrations are not elevated at this depth, indicating it might be a preservation problem) or whether it represents a localized zone of in situ evaporation (water contents in this zone are some of the lowest measured).

In addition to the initial stable isotope sampling, isotope samples were obtained during two of the transient flow events in the Well 16-02655 (March and July 1999). The  $\delta^{18}$ O and  $\delta$ D results were –12 and –8 permil and –83 and –76 permil, respectively, indicating a shift from highly evaporated to more meteoric values.



**Figure 4.4-12. Pore water chloride profiles for Well 16-02669 (90s Line Pond), Well 16-02665 (Martin Spring Canyon), and Well 16-02667 (SWSC Cut); core collected in 1997** 



**Figure 4.4-13. Cumulative water versus cumulative chloride for Well 16-02669 (90s Line Pond), Well 16-02665 (Martin Spring Canyon), and Well 16-02667 (SWSC Cut); core collected in 1997** 



**Figure 4.4-14. Stable isotope (**δ**18O) and water content profiles for Well 16-02669 (90s Line Pond); core collected in 1997** 



**Figure 4.4-15. Stable isotope (**δ**18O) and water content profiles for Well 16-02665 (Martin Spring Canyon); core collected in 1997** 





### **4.4.2.2.10 Vadose Zone and Source Interpretation**

This section summarizes the interpretation of contaminant sources to the unsaturated and transientsaturated portions of the mesa vadose zone. Initial discussion of contaminants focuses on the unsaturated portion of the vadose zone, defined as that zone above the transient saturated zones. Chloride-based residence times in the unsaturated parts of the vadose zone indicate little downward movement of water and contaminants over much of the mesa (e.g., areas not directly underneath ponds or drainages). Thus, most of the mesa vadose zone does not appear to be an effective pathway for recharge and deep contaminant transport. This result is not surprising given the semiarid conditions at the site.

This conclusion does not hold for the entire mesa because the observations of HE contaminated transient saturation in the 90s Line Pond and Martin boreholes, which indicates recharge to the transient saturated zones in less than or about fifty years (the HE facilities began operation in the late 1940s). The stable isotope data from the saturated zones provide an important clue to resolve the apparent inconsistency between the long residence times indicated by the chloride data and the short residence times indicated by the presence of HE contamination in the transient saturated zones. The large isotope values from the saturated zones (Figure 4.4-17) indicate the waters have undergone substantial evaporation. It is unlikely the waters were evaporated in situ because the zones are wet and because pore waters above and below the saturated zones do not show any evidence of strong evaporation (with one exception discussed earlier).

In reviewing the possible sources of water that have undergone substantial evaporation (having large isotope values) on the mesa, most outfall and discharge waters are not strongly evaporated, having  $\delta^{18}O$ values of about –10.5 permil and δD values of about –76 permil or less (Blake 1995, 49931; LANL 1996, 55077). The source of the discharged water was the regional aquifer, and only minor evaporation occurred during HE processing. Thus, the isotopic composition of outfall water is not consistent with the large values observed in the 90s Line Pond and Martin borehole transient saturated zones. The only known sources that are consistent with the observed saturated zone values are the 90s Line Pond and 30s Line Ponds [SWMU 16-007(a)], and V-Site Pond [SWMU 16-029(x)] disposal lagoons on the mesa. These surface impoundments are subject to significant evaporation, particularly in the summer. A limited set of stable isotope data is available from the 90s Line Pond, and values show evaporative effects similar to the borehole waters (e.g., 6.8 and 2 permil  $\delta^{18}$ O and  $\delta$ D, respectively). Thus, the stable isotope data indicate the ponds are a likely source of fast recharge and HE contamination to the transient saturated zones encountered in the 90s Line Pond and Martin boreholes. These sources are also consistent with chloride and HE concentrations in the transient saturated zones (LANL 1996, 55077).

Both boreholes were drilled in the vicinity of disposal lagoons, which supports the interpretation of a ponded water source. It also indicates there is a lateral component to the flow since the boreholes were not drilled directly within any of the ponds. The presence of HE in the saturated zones and absence of HE above and below the saturated zones, the stable isotope and water content distributions in the boreholes, and observed subhorizontal fracturing in core samples from the transient saturated zones are additional evidence for a lateral flow component. The timing of flows into the Martin borehole and the observed shift to negative isotope values indicate the transient nature of flow and transport is seasonally or event controlled (although flow was probably more regular during the period of active discharge into the ponds). All of the recent flow events were associated with relatively large winter/spring snowmelt/precipitation events or summer "monsoonal" rains. It is likely that even though the pond waters have evaporative isotope values over most of the year, the values shifted to more meteoric values during the winter and during high-volume wastewater discharges. Thus, it is not surprising the values in the borehole vary over time. It is also likely there may be some vadose zone mixing between older contaminated pond waters and newer recharge as indicated by the response to snowmelt/precipitation events.



**Figure 4.4-17. Meteoric water diagram for data from the transient saturated zones in Well 16-02669 (90s Line Pond) and Well 16-02665 (Martin Spring Canyon)** 

# **4.4.3 Data Summary and Interpretation**

This section (1) reviews results from previous sections and summarizes the COPCs in the TA-16 subsurface and (2) discusses the extent of these COPCs in the vadose zone saturated system manifested in the TA-16 springs.

# **4.4.3.1 Major COPCs**

Table 4.4-31 summarizes the retained COPCs. The major COPCs are aluminum, barium, boron, lead, manganese, and RDX. It should be noted however, that aluminum, lead, and manganese were eliminated as COPCs for the springs based on a geochemical analysis. Many of the other COPCs are detected in only a few samples. Some, like nitrate and perchlorate, may represent post-validation data issues such as seemingly incorrect reporting units (nitrate; see Section 4.4.2.1.1) or are only transient. Perchlorate, for instance, is only detected in three sampling rounds for which it was analyzed (see Table 4.4-1). A complete list of COPCs for the springs, 90s Line Pond, and the intermediate-depth boreholes includes aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, cesium, chromium, cobalt, copper, cyanide, lead, manganese, mercury, nickel, nitrate + nitrite, perchlorate, rubidium, selenium, silver, thallium, uranium, vanadium, zinc, dinitrobenzene[1,3-], methylene chloride, nitrobenzene, RDX, trichloroethene, and trinitrotoluene[2,4,6-]. These COPCs are carried forward into risk analysis based on a comparison to NMWQCC, EPA MCL, or EPA Region 6 PRG standards (where they exist).

# **4.4.3.2 Extent of Contamination**

HE and other contaminants are present in all three springs, in 90s Line Pond, and in the intermediatedepth perched aquifer sampled at TA-16. The traditional concept of extent of contamination (decreasing trends) is not relevant in the subsurface system because there is no evidence for a distinct, coherent plume impacting the springs. Rather, the system is dominated by a combination of rapid pathways and base-flow recharge with discontinuous subsurface saturated zones (see section 5), and it is important to understand the movement of contaminants in the saturated zones and the interconnectivity of the saturated zones with other components of the conceptual model. Because the springs are discharged through the mesa vadose zone, there must be contamination upgradient along subsurface flow paths. In addition, the intermediate-depth perched aquifer well characterization and geophysical surveys indicate that the flow paths are heterogeneous, both temporally and spatially. Based on the oxygen and deuterium stable isotope results, evaporative effects are observed in the 90s Line Pond, Well 16-02665 (Martin Spring Canyon), and Well 16-02669 (90s Line Pond), but not in the springs. This is evidence that contamination extends from ponded areas into certain areas of the mesa vadose zone, but that the subsurface is heterogeneous. Although the 260 outfall was connected to Burning Ground and SWSC Springs based on tracer data, there is no evidence at this time that ponds recharge the mesa vadose zone perched aquifer directly beneath TA-16.

# **4.5 Implications for the TA-16 Hydrogeologic Conceptual Model**

# **4.5.1 Potential Contaminant Sources**

The water chemistry of the TA-16 springs (Burning Ground, SWSC, and Martin Springs), shallow perched groundwater, and 90s Line Pond is distinct from that of background springs (i.e., Apache Spring, Cañon de Valle Spring, etc.) and likely represents contamination resulting from operations at TA-16. Not only metals and HE were elevated, but also major cations and anions such as calcium and chloride.

	<b>Water</b>							
<b>Chemicals Retained as COPCs</b> for SWMU 16-021(c)-99 <b>Subsurface System</b>	<b>Springs (see</b> Tables 4.4-3, 4.4-6, and 4.4-9)	90s Line Pond (see Tables 4.4-12, 4.4- 15, and 4.4-18)	Intermediate-Depth <b>Perched Aquifer</b> (see Tables 4.4-24, 4.4-27, and 4.4-30)					
<b>Inorganic Chemicals</b>								
Aluminum	$---a$	$\bullet^{\circ}$	$\bullet$					
Antimony	$\bullet$	$\bullet$	$\bullet$					
Arsenic	---	$\bullet$	$\bullet$					
<b>Barium</b>	$\bullet$	$\bullet$	$\bullet$					
Beryllium	---	$\bullet$	$\bullet$					
Boron	$\bullet$	---	$\bullet$					
Cadmium	---	$\bullet$	$\bullet$					
Cesium	$\bullet$	$N\overline{A^c}$	<b>NA</b>					
Chromium	---	$\bullet$	$\bullet$					
Cobalt	$---$	$\bullet$	$\bullet$					
Copper	$---$	---	$\bullet$					
Cyanide (Total)	$\bullet$	---	---					
Lead	---	$\bullet$	$\bullet$					
Manganese	$---$	$\bullet$	$\bullet$					
Mercury	$\bullet$	$\bullet$						
<b>Nickel</b>	---	$---$	$\bullet$					
Nitrate-Nitrite as N	$\bullet$	---						
Perchlorate	$\bullet$	$---$	---					
Rubidium	$\bullet$	NA	$\overline{NA}$					
Selenium	---	$\bullet$	$\bullet$					
Silver	$---$	$---$	$\bullet$					
Thallium	$\bullet$	$\bullet$	$\bullet$					
Uranium	$\bullet$	$\bullet$	---					
Vanadium	---	$\bullet$	---					
Zinc	$---$	$---$	$\bullet$					
<b>Organic Chemicals and HE</b>								
Dinitrobenzene[1,3-]	$\bullet$	---	---					
Methylene Chloride	---	---	$\bullet$					
Nitrobenzene	$\bullet$	---						
<b>RDX</b>	$\bullet$	$\bullet$	$\bullet$					
Trichloroethene			0					
Trinitrotoluene[2,4,6-]	$\bullet$	---	$\bullet$					

**Table 4.4-31 Table of Retained COPCs for SWMU 16-021(c)-99 Subsurface System** 

a <sub>---</sub> = Chemical was analyzed for but eliminated as a COPC for this subsurface system component.<br>**b ●** = Chemical retained as a COPC for this subsurface system component.<br><sup>C</sup> NA = Not Analyzed.

The following generalizations can be made about the data for the TA-16 springs.

- The TA-16 springs represent higher ionic strength fluids than the background springs such as Apache Spring, Cañon de Valle Spring, Water Canyon Spring Gallery, Pine Spring, and Seven Springs (Blake 1995, 49931).
- Martin Spring is geochemically distinct compared with the other two springs, with higher concentrations of RDX, nitrate, calcium, and chloride and a lower RDX/HMX ratio.
- Boron in Martin Spring is over an order of magnitude higher in abundance than in the SWSC Spring, Burning Ground Spring, or in the background springs. Boron in Martin Spring probably represents anthropogenic contamination. Possible sources of boron include (1) locales where the HE boracitol (a mixture of boric acid and TNT) was processed, such as V-Site and Building 260 and (2) the TA-16 laundry facilities, which formerly discharged to the TA-16 Waste Water Treatment Plant (WWTP).

Possible sources of high ionic strength fluids (i.e., enriched in elements such as calcium and chloride) are listed below:

- The TA-16 steam plant and its derived waters in the steam plant and 90s Line Pond drainage (Figure 4.5-1). Analyses of the steam plant drainage alluvial borehole (Well 16-02655), provided in the Phase II RFI report (LANL 1998, 59891), show high calcium, sodium, magnesium, and chloride. Analyses of the 90s Line drainage, which received discharge from the TA-16 steam plant (LANL 1996, 55077, p. C-8), show high silicon dioxide (145,730 and 150,230 µg/L), sodium  $(134,000$  and  $154,000$   $\mu q/L$ ), bicarbonate  $(311,000$  and  $345,000$   $\mu q/L$ ), and total dissolved solids (TDS) (636,000 and 749,400 µg/L). All of these levels are higher than the levels measured in TA-16 springs.
- The TA-16 WWTP. Two analyses of water from the TA-16 WWTP show high TDS (319,500 and 440,100 µg/L), sodium (117,000 and 80,900 µg/L), calcium (30,200 and 23,500 µg/L), silicon dioxide (76,610 and 83,030  $\mu$ g/L), chloride (216,000 and 136,000  $\mu$ g/L), and bicarbonate (101,000 and 93,200 µg/L) (LANL 1996, 55077). The WWTP received sewage effluent from across TA-16 and discharged treated effluent until it was decommissioned in 1992. The WWTP is located within 1000 ft of Martin Spring (Figure 4.5-1).
- Deep well water derived from the Puye Formation and Santa Fe Group. A large number of well and spring samples (Blake 1995, 49931, pp. 10–12) derived from within the Puye and Santa Fe Groups contain high naturally occurring ionic strength fluids with high TDS and associated high values of sodium, bicarbonate, and other major cations and anions.
- Surface waters that include a component of road salt. TA-16 roads are frequently salted during the winter months. Runoff from these salted roads is at higher ionic strength than typical precipitation and water from pristine springs without anthropogenic inputs.
- Evaporation in 90s Line Pond may result in recharge of higher ionic strength waters.





Both TA-16 process water (LANL 1996, 55077, p. C-7) and local precipitation (Adams et al. 1995, 47192, pp. 7–9) have TDS less than 200,000 µg/L. During interaction with tuff and sediment, these process waters or rainwaters could dissolve additional constituents and achieve higher ionic strengths. However, it is unknown if such interactions would yield higher TDS values than observed in background springs, which presumably undergo similar precipitation/rock interactions.

The 260 outfall is the most obvious source for HE and other contaminants at SWSC Spring and Burning Ground Spring. Barium, nitrate, and RDX are all present in the source area outfall region. The distinct differences in major element chemistry between SWSC Spring and Burning Ground Spring versus Martin Spring indicate the former two springs are part of a related saturated system, whereas the latter spring may have different/additional recharge sources and may interact with different/additional contaminant sources. Multiple recharge sources at TA-16 are likely. Isotope data indicate Martin Spring has a different recharge source than the other two springs (see section 4.4.2.1.7 and section 5), with a greater percentage of recharge occurring on the mesa top.

Regardless of the source, some breakdown of RDX must be occurring in the subsurface, as RDX breakdown products MNX, DNX, and TNX were occasionally detected in the springs (see Table 4.4-4).

The 90s Line Pond and the springs share many COPCs, though concentrations are higher at 90s Line Pond, particularly in unfiltered samples. It is not surprising the 90s Line Pond may have higher contaminant concentrations, as it is subject to evaporative effects and receives inputs of surface particulate materials. These results, however, cannot be used to infer the 90s Line Pond is a significant source of contaminants to the springs. Isotope and water balance considerations indicate this is unlikely (see section 5).

Well 16-02665 (Martin Spring Canyon) has several COPCs in common with Martin Spring, including elevated levels of boron. Whereas the perched zones in the well are hydrologically lower than Martin Spring (and therefore cannot feed the spring), a common contaminant source may be implicated. Based on isotopic evidence (see section 4.4.2.2.9), it does not appear Martin Spring is a source of water for Well 16-02665.

In the CMS plan for SWMU 16-021(c)-99 (LANL 1998, 62413.3), it was proposed that mixing models for the various potential contaminant and background sources would be developed. This is difficult given the fact there has been a low-flow regime for most of the Phase III RFI study period. Observation that the RDX/HMX ratios for the springs are consistent with the solubilities for these two compounds (see Table 5.2.1 in section 5) could be used in the mixing model. This ratio could indicate a saturated solution of RDX (e.g., process waters and waters that have had prolonged contact with HE in sediment and soil) being diluted by background and other waters. The solubility of RDX is 60 mg/L. The highest spring RDX concentration is 330 µg/L. This concentration indicates spring waters contain less than 1% of the saturated solution indicated by the solubility (assuming the diluting waters contain no RDX). Process waters from the 260 outfall were measured for RDX prior to the outfall being shut off. RDX concentrations were 484 µg/L (LANL 1996; 55077). Conducting a similar mixing calculation with the same assumptions (dilution by waters with no RDX) results in <1% of the spring water representing process water. The RDX concentration of 484 µg/L for the 260 outfall may not be representative of the entire history of discharge. The highest RDX concentrations were found in Well 16-02712 (now plugged and abandoned) below the 260 outfall, where concentrations as high as 2490 µg/L were detected (Sample ID RE16-98-3026, as presented in Appendix G-2). This higher value indicates approximately 4% of the water in the borehole is process water, based on the assumptions above. These calculations provide minimum percentages of process waters given the assumption of RDX saturation in such fluids.

#### **4.5.2 Spring and Contaminant Dynamics**

In the Phase II RFI report (LANL 1998; 59891), flow and concentration data are used to conclude that multiple recharge zones are tapped during increased flow to the springs. Based on spring hydrograph responses during the 1997 monsoon season, at least three distinct recharge sources impact the springs. Three plausible candidates for these recharge sources are (1) direct runoff into the spring catchments, with a response time of a few hours; (2) an interflow pathway, with a response time of 1 to 2 days; and (3) a subsurface pathway, with a several-week response time. During the Phase III RFI study period, however, a period of low flows and overall decreases in flow occurred; therefore, these findings cannot be verified.

Figures 4.5-2a–f show the effect of flow on contaminant mass (i.e., concentration multiplied by flow) and Figures I3-7, I3-8, I3-20, I3-21, I3-33, and I3-34 show the relationship between contaminant concentration and flow rates for barium and RDX.

Barium and RDX masses increase over time at Martin Spring (Figures 4.5-2a, 4.5-2b), though the trend in RDX mass is largely a function of lower values for the data collected prior to the June 1998. This is unexpected during a period of decreasing flow. Some increase in concentration of these contaminants might be expected due to evaporative concentration during low flow periods, but this effect alone would result in a flat trend (i.e., if flow and concentration were related in a 1:1 manner such that a doubling of flow led to a halving of concentration or vice versa). Several explanations are possible. The first is that the center of mass of a contaminant "plume" may be approaching Martin Spring, thereby leading to higher contaminant concentrations. Whereas the temporal trends in barium and RDX concentrations at Martin Spring (Figures 4.4-1a and 4.4-4a) are not statistically significant, some of the highest values are found in the most recent data. However, the current conceptual model does not support a coherent contaminant plume migrating to the springs.

Alternatively, bound contaminants may be desorbed from the tuff as a result of matrix diffusion during long drought periods, thereby increasing pore water concentrations. These higher concentration pore waters are then flushed during subsequent wet periods. Another explanation is that rapid recharge through short pathways (fractures) have been shut off due to the drought (see section 5). Water flow through these pathways may have had a "dilution" effect. During high-flow events, increased amounts of barium appear to be flushed from the system. Since the concentration of barium decreases with increased flow (Figure I3-7), this increase in mass is likely due to a greater area of contamination being flushed prior to discharge at the spring. As mentioned above, due to desorption, the pore water may also have increased concentrations. RDX concentrations also decrease during high flow (Figure I3-8), but no large difference in RDX mass is observed during these events (Figure 4.5-2b). Finally, it is possible that water is concentrated in more contaminated zones during drought conditions.

SWSC Spring shows no significant trends in barium or RDX mass versus time (Figures 4.5-2c, 4.5-2d). However, the mass of both contaminants is generally higher during high-flow regimes, indicating flushing of both contaminants from a higher concentration source area (the subsurface flow paths may increase in size during high-flow events leading to flushing of macropores with high contaminant concentrations, or more of the source area may be impacted by infiltrating water). Barium concentrations at this spring are not significantly affected by flow (Figure I3-20), but RDX concentrations increase during high-flow events (Figure I3-21). The latter observation is consistent with flushing of macropores with high contaminant concentrations or with dissolution of solid HE during high-flow events. The SWSC system is highly complex. It is near the source area, is susceptible to effects of the IM (if any), and has undergone a complete drying. Because these factors have counteracting effects on contaminant mass, no temporal trends in mass are observed.



**Figure 4.5-2a. Mass of barium versus time at Martin Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 



**Figure 4.5-2b. Mass of RDX versus time at Martin Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 



**Figure 4.5-2c. Mass of barium versus time at SWSC Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 



**Figure 4.5-2d. Mass of RDX versus time at SWSC Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 



**Figure 4.5-2e. Mass of barium versus time at Burning Ground Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 



**Figure 4.5-2f. Mass of RDX versus time at Burning Ground Spring. Only detected values are shown and used for statistical analysis. Sample values from high-flow periods are shown in red. Regression equation and significance level are shown.** 

Burning Ground Spring shows overall decreases in barium mass over time (Figure 4.5-2e), but no significant trends in RDX mass (Figure 4.5-2f). High-flow periods are generally marked by increases in barium and in RDX (at least in the latter two years of the study). Barium concentration is positively correlated with flow (Figure I3-33), whereas RDX shows no such trend (Figure I3-34). Decreased flow over time should result in decreased contaminant mass (assuming evaporative effects on concentration are not completely offsetting the flow effect). In addition to the overall decreased flow, the flow paths may be concentrated into areas already well flushed of contaminants. This pattern is interrupted only during high-flow events. The IM may also be having an effect, but there is no definitive evidence to support this.

Figures 4.5-3a–i, I3-9 through I3-13, I3-22 through I3-26, and I3-35 through I3-39 show concentration versus concentration plots and Figures 4.5-4a–c show mass versus mass plots, with high-flow events marked. Together these plots demonstrate whether contaminants are correlated with one another or with major cations and anions, during low and high-flow periods.

For Martin Spring, barium and RDX (Figure 4.5-3a), RDX and HMX (Figure 4.5-3b), RDX and chloride (Figure I3-9), and RDX and calcium (Figure I3-10) are all positively correlated with lowest concentrations occurring during high-flow events. Barium and RDX mass are also positively correlated, though barium falls off the trend during high-flow events (see previous discussion of barium/flow dynamics) (Figure 4.5-4a). These facts indicate a common source for all contaminants and that the contaminant source, or at least some portion of the recharge water feeding the spring, has high ionic strength in elements like calcium and chloride. Martin Spring shows a statistically inverse relationship between RDX and filtered iron (Figure I3-11), with highest iron concentrations occurring during high-flow events. The most likely explanation for this is that during high-flow events there is preferential flushing of very small colloids (< 0.45 microns) of iron. Unfiltered and filtered iron are positively correlated (Figure I3-13), which is consistent with a colloidal form for both phases. Aluminum is positively correlated with iron (Figure 4.5-3c), with both being highest during high-flow events, consistent with flushing of colloids.

At SWSC Spring, RDX and HMX are positively correlated with highest concentrations occurring during high-flow events, indicating they are derived from the same source area (Figure 4.5-3e). Flow-related RDX concentration effects are discussed above. RDX is positively correlated with chloride (Figure I3-22), but no significant relationship with calcium exists (Figure I3-23). The only other significant concentration relationship found for SWSC Spring was between iron and aluminum (Figure 4.5-3f). Barium and RDX mass is significantly positively correlated (Figure 4.5-4b) with highest masses during high-flow periods, consistent with flushing of spatially larger flow paths including macropores with high contaminant concentrations.

At Burning Ground Spring, RDX and HMX are positively correlated (Figure 4.5-3h), indicating a common source. Relationships with flow are unclear. RDX is positively correlated with chloride and calcium (Figures I3-35, I3-36), similar to Martin Spring. Also similar to Martin Spring, unfiltered and filtered iron are positively correlated (Figure I3-39) as are iron and aluminum (Figure 4.5-3i). Barium mass and RDX mass are positively correlated (Figure 4.5-4c) with barium being higher relative to the main trend during highflow events for reasons discussed above.



**Figure 4.5-3a. Plot of barium versus RDX at Martin Spring. Red diamonds represent high-flow events.** 







**Figure 4.5-3c. Plot of iron versus aluminum at Martin Spring. Red diamonds represent high-flow events.** 







**Figure 4.5-3e. Plot of RDX versus HMX at SWSC Spring. Red diamonds represent high-flow events.** 



**Figure 4.5-3f. Plot of iron versus aluminum at SWSC Spring. Red diamonds represent high-flow events.** 



**Figure 4.5-3g. Plots of barium versus RDX at Burning Ground Spring. Red diamonds represent high-flow events.** 



**Figure 4.5-3h. Plot of RDX versus HMX at Burning Ground Spring. Red diamonds represent highflow events.** 



**Figure 4.5-3i. Plot of iron versus aluminum at Burning Ground Spring. Red diamonds represent high-flow events.** 



**Figure 4.5-4a. Plots of barium mass versus RDX mass at Martin Spring. Red diamonds represent high-flow events.** 



**Figure 4.5-4b. Plots of barium mass versus RDX mass at SWSC Spring. Red diamonds represent high-flow events.** 



#### **Figure 4.5-4c. Plot of barium mass versus RDX mass at Burning Ground Spring. Red diamonds represent high-flow events.**

### **4.5.3 Summary of Findings and Implications to the Conceptual Model**

- 1. The 260 outfall is connected to SWSC Spring and Burning Ground Spring (see the results of the tracer study in section 2). SWSC Spring and Burning Ground Spring have similar chemistry although SWSC Spring has somewhat higher barium concentrations and a somewhat higher RDX/HMX ratio. The latter observation indicates SWSC Spring is receiving contamination from a somewhat deeper and older part of the TA-16-260 source area, as RDX was used more prevalently relative to HMX in the past. The proposed connection of the 260 outfall to Martin Spring is much less obvious. The high boron concentrations could reflect the fact that Martin Spring is receiving older contamination from the 260 outfall when boracitol was discharged. On the other hand, the lower RDX/HMX ratios indicate a more recent source. It is likely a component of the contamination at Martin Spring is from a different source, such as the 30s Line Ponds (SWMU 16-007[a]), the 90s Line Pond (SWMU 16-008[a]-99), V-Site Pond (SWMU 16-029[x]), the TA-16 WWTP, or other World War II-era drainages.
- 2. There are both rapid pathways and longer residence-time pathways influencing the springs. Different sources of recharge water, including process and background water, combine to generate the discharge at a given spring. These sources vary among springs and over time.
- 3. Contaminant fluxes/masses are related to discharge rates. Generally during high-flow periods the mass of barium and RDX increased at all three springs. This is important because even though decreases are observed in the mass of barium through time at Burning Ground Spring, this trend may be reversed during a wetter precipitation period.
- 4. No conclusive evidence is found for an influence of the IM to date.

### **5.0 CONCEPTUAL MODEL DEVELOPMENT**

#### **5.1 Overview**

The conceptual model for the 260 outfall describes the distribution of contamination in the context of local geologic, geochemical, and hydrologic features and processes. Previous sections have presented the results of the Phase III RFI field sampling for key components of the system, including the SWMU 16- 021(c)-99 source area, the mesa vadose zone and canyon springs, and the Cañon de Valle and Martin Spring Canyon alluvial systems. In this section, these results are used to update the comprehensive conceptual model of contaminant distribution. The model addresses the processes that resulted in the present-day distribution of contaminants and offers insight into future contaminant transport.

At TA-16, the combination of relatively wet mesa and canyons, heterogeneous geologic units, multiple flow paths, different types of flow behavior, and multiple contaminant sources results in a hydrogeologic conceptual model that must incorporate multiple pathways and processes. Due to its complexity, the TA-16 conceptual model continues to display uncertainties associated with the distribution of contaminants, particularly within the mesa and Cañon de Valle vadose zones.

The conceptual model, depicted in Figure 5.1-1, applies to a roughly triangular area that is bounded on the north by Cañon de Valle, on the south by Water Canyon, on the west by the Pajarito fault zone, and on the east by the confluence of Water Canyon and Cañon de Valle (see Figure 5.2-1), an area of roughly 3 mi<sup>2</sup> miles. In addition to the TA-16-260 outfall, this area encompasses other historical contaminant sources such as MDA R and MDA P. Thus, the conceptual model applies to all historical contaminant sources at TA-16, particularly those affecting waters. Within the conceptual model, contaminant transport pathways are associated with groundwater flow in tuff, sediment, and waters. Groundwater flow systems occur in many different forms; these include fracture and surge bed systems in tuff, alluvial groundwater in Cañon de Valle and Martin Spring Canyon, SWSC Spring, Martin Spring, Burning Ground Spring, Fishladder Seep, Peter Seep, and the 90s Line Pond. The duration and flow rate of groundwater differs in these systems, ranging from perennial flow in the Cañon de Valle alluvial system to episodic stormwater flow in mesa vadose zone fractures.

Figure 5.1-1 shows the key components of the conceptual model centered at the SWMU 16-021(c)-99 source area, as defined by Regional Aquifer Well R-25:

- the SWMU 16-021(c)-99 source area and surge bed (see component 1 on the figure),
- the mesa vadose zone, consisting of nonfractured and fractured tuff which extends to the canyon bottom (see 2 on the figure),
- canyon alluvial sediment (see 3 on the figure),
- canyon springs (see 4 on the figure),
- canyon surface water (see 5 on the figure),
- canyon alluvial groundwater (see 6 on the figure),
- the deep vadose zone, consisting of nonfractured and fractured tuff which extends from the canyon bottom to the top of the regional aquifer and includes the intermediate-depth perched aquifer (see 7 on the figure), and
- the regional aquifer (see 8 on the figure).



**Figure 5.1-1. Conceptual model of hydrogeological and contaminant transport for TA-16 and SWMU 16-021(c)-99** 

While the regional aquifer is not included in the scope of the Phase III RFI, key results from the installation and sampling of Well R-25 are important for a general understanding of the conceptual model. In addition, although this figure does not include MDA R or MDA P, which are historical sources of contamination, the figure depicts the major components of the subsurface that can be considered contaminant transport pathways for these other historical source areas as well. Similarly, while Martin Spring Canyon is not shown on this figure, contaminant pathways such as springs, alluvial sediment, alluvial groundwater, and fracture pathways to deeper zones apply there also.

In general, the overall conceptual model presented in the Phase II RFI still applies on a site-wide basis. Phase III conceptual model changes have largely been refinements that have reduced data uncertainties for the CMS process. The following sections describe the key components of the conceptual model, along with the supporting data. For reference, a brief summary of the Phase II conceptual model (LANL 1998, 59891) for each component is also presented.

#### **5.2 Phase III Conceptual Model**

### **5.2.1 Component 1—TA-16-260 Outfall Source Area and Surge Bed**

The TA-16-260 outfall source area and underlying surge beds are labeled component 1 on the conceptual model (Figure 5.1-1).

The conceptual model presented in the Phase II RFI report (LANL 1998, 59891) included three principal contaminant transport pathways from the TA-16-260 source area: (1) transport via surface runoff to Cañon de Valle; (2) transport via lateral shallow subsurface flow (interflow) surge beds to Cañon de Valle; and (3) infiltration to the mesa vadose zone hydrologic system through preferred pathways, such as fractures, in the Bandelier Tuff.

The 260 outfall discharges during the past 50 years at SWMU 16-021(c)-99 served as a source for HE and inorganic contamination found throughout the site (LANL 1998, 59891). The principal contaminants in 260 outfall sediment were barium (up to 20,000 ppm) and HE (greater than 200,000 ppm). Historically, discharge from the sumps at Building 260 to the 260 outfall was reportedly as high as several million gal./yr (LANL 1994, 76858). The 260 source area comprises a well-defined upper drainage channel that was fed directly by the building sumps, a former settling pond, and a drainage channel that leads to Cañon de Valle. HE contamination in the 260 outfall and drainage area has been recognized since at least 1960 when the first soil samples from the 260 outfall were analyzed.

The former settling pond and associated soil, which were removed during the 2000 IM (LANL 2002, 73706), measured approximately 50 ft long by 20 ft wide and were located within the upper drainage channel, approximately 45 ft below the 260 outfall. The drainage channel runs approximately 600 ft northeast from the 260 outfall to the bottom of Cañon de Valle. A 15-ft near-vertical cliff is located approximately 400 ft from the 260 outfall and marks the break between the upper and lower drainage channels. Prior to the IM, the upper part of the drainage channel (above the cliff) contained little vegetation and relatively little accumulated soil and sediment. The lower part of the drainage channel (below the cliff), which is steep and rocky, contained thick pockets of sediment.

Borings installed in the former settling pond area revealed the presence of surge beds underlying the area at depths of approximately 17 and 45 ft. Other surge beds containing low-level concentrations of HE were encountered during the Phase II RFI drilling in the area around the 260 outfall (LANL 1998, 59891). These surge beds (granular tuff with a sand-like texture) possess increased porosity and hydraulic conductivity, and they contain elevated concentrations of HE. The surge beds represent contaminant

transport pathways leading away from the TA-16-260 source area. The number, lateral extent, and continuity of the surge beds are unknown.

One of the most substantial changes to the site since the 1998 Phase II RFI was the removal of a large quantity of contaminated soil from the TA-16-260 outfall and pond area during the IM (LANL 2002, 73706). More than 1300 yd<sup>3</sup> of contaminated material containing approximately 8500 kg of HE were removed from this area.

The surge beds were not excavated during the IM. Results from surge bed borings installed during the IM (LANL 2002, 73706) and the Phase III RFI indicate that substantial contamination resides within surge beds beneath the former source area. It is likely that other similarly contaminated surge beds exist within the mesa vadose zone. Low-level concentrations of HE in fractured and welded tuff, other than surge beds, were also detected during Phase II RFI drilling (LANL 1998, 59891).

Contaminant transport from the 260 outfall and surge bed area is a direct result of the 260 outfall discharges of contaminated water to Cañon de Valle and the infiltration of contaminated water into underlying tuff along the 260 outfall drainage. Once they infiltrated, TA-16-260 outfall water and its contaminants likely migrated from the source area through the nonfractured and fractured underlying tuff as well as the surge beds, with the latter two pathways dominating because of their relatively higher permeability.

The potential for infiltration was likely highest within the 260 outfall former settling pond, where HE sediment contamination was high and where the ponding of water resulted in a hydraulic driving force for enhanced vertical infiltration. The presence of elevated levels of HE compounds detected within the underlying surge bed confirms this enhanced contaminant migration from the former settling pond.

The IM removed all soil from the former settling pond, allowing inspection of previously buried soil/tuff contact. Small fractures in the tuff are apparent, although their characteristics, such as density and precise aperture, were not formally investigated. The IM substantially reduced the quantities of HE and barium throughout the source area and drainage channel. Residual HE contamination remains in pockets of soil distributed along the drainage channel. Sampling of these pockets indicated the presence of HMX, RDX, TNT, and barium. HMX was found at concentrations as high as 2000 mg/kg; barium, at concentrations as high as 8200 mg/kg; and RDX, at concentrations as high as 1200 mg/kg. Although it contains elevated concentrations, the total volume of residual contaminated soil is estimated to be less than 100 yd<sup>3</sup>. Nevertheless, this residual soil represents a continuing source for Cañon de Valle contamination.

# **5.2.2 Component 2—Mesa Vadose Zone**

The mesa vadose zone lies between the mesa land surface and the bottom of the canyons (Figure 5.1-1). In the Phase II RFI report, the principal contaminant flow paths within the mesa vadose zone were hypothesized to be ribbon-like structures (LANL 1998, 59891). This description, while not geologically specific, reflects a mesa vadose zone flow regime that is dominated by a sporadic distribution of surge beds and fractures, both of which possess higher permeability than the surrounding nonfractured tuff. The Phase II RFI also indicated that: (1) these preferential flow paths predominate near the contact between units 3 and 4 of the Bandelier Tuff; (2) flow along these preferential flow paths is intermittent and responds to rainfall and snowmelt events; and (3) groundwater recharge areas for the preferential flow paths may include the Pajarito fault zone, the steam plant drainage, and the 90s Line Pond. This conceptual model for the mesa vadose zone remains valid, but it has been refined based on the Phase III investigations.
As part of the Phase II RFI, five wells were drilled to depths between 91 ft and 207 ft in order to characterize the intermediate-depth perched aquifer and to define the nature and extent of contamination (Figure 4.4-10 of this report). The initial results of the drilling were reported in the Phase II RFI report (LANL 1998, 59891). The Phase III RFI data provide an updated assessment of the mesa vadose zone behavior based on chloride and stable isotope tracers, results of hydraulic testing of core, and groundwater chemistry data from Well 16-02665 (Martin Spring Canyon) samples that were collected after completion of the Phase II RFI (post-1998).

Tuff samples from the intermediate-depth well boreholes that were installed within the mesa vadose zone indicate no contamination in the subsurface intervals; the exception is BH 16-06370 (an uncased borehole drilled in the 260 outfall former settling pond) (LANL 1998, 59891; LANL 2002, 73706). These results indicate that mesa vadose zone contamination is primarily concentrated beneath source areas such as the former and current ponds and drainages on the mesa top, with lesser inventories of contamination present elsewhere. As discussed in section 4.4.2.2.2, Intermediate-Depth Perched Aquifer Wells 16-02665 (Martin Spring Canyon) and 16-02669 (90s Line Pond) have, on occasion, contained contaminated groundwater. It appears that disposal ponds on the mesa, or the 260 former settling pond, affected these zones and that there is lateral movement of water and contaminants in the subsurface. Thus, while most of the contaminant inventories are probably directly below or near source areas, lower concentration contaminant inventories are present away from the source areas within the mesa vadose zone.

The conclusion that the major portion of the mesa contaminant inventory resides in the vicinity of the source areas is reinforced by water content sampling results. These indicate that much of the vadose zone away from the source areas is relatively dry, and the chloride results from intermediate-depth well show that vadose zone residence times away from the source areas are more than 1000 yr (section 4.4.2.2.8; Broxton et al. 2002, 72640). In other words, because the source areas represent locations where substantial water was added to the mesa, while the rest of the mesa remained dry, a substantial portion of the vadose zone contaminant inventory resides in the subsurface below the source areas.

In terms of transport, Wells 16-02665 and 16-02669 provide information about how rapidly water and contaminants have been transported downward into the mesa beneath the source areas. Data from these wells show that HE contaminants have moved from the top of the mesa down to at least 130 ft bgs in 50 yr or less. The breakthrough of bromide tracer at SWSC Spring and Burning Ground Spring within a few months of its placement in the settling pond is additional evidence for rapid contaminant transport along preferred pathways in the mesa vadose zone. Finally, the presence of HE contamination in the approximately 700-ft perched aquifer at Regional Aquifer Well R-25 (LANL 2003, 75986.2) indicates that these transport pathways may extend from the mesa (or canyon bottom) downward to the 700-ft perched aquifer.

The variable concentrations and presence of contaminants detected in the vadose zone at TA-16 are typical of fracture (and surge bed) controlled transport. This fact has important implications for the CMS decision process. First, it is not possible at the present time to accurately quantify the inventory of contaminants in the mesa vadose zone. Future characterization efforts at TA-16 may provide a better estimate of contaminant inventories, although it is unlikely that a detailed inventory will ever be achieved. Second, the contamination may not be accessible for remediation.

Other uncertainties in the mesa vadose zone conceptual model remain: the effects from the 2000 Cerro Grande fire and the current forest thinning, both of which may have altered the runoff/recharge hydrology on the mesa.

## **5.2.3 Component 3—Alluvial Sediment in Cañon de Valle and Martin Spring Canyon**

Alluvial sediment is present in both Cañon de Valle and Martin Spring Canyon (Figure 5.1-1). The Phase II RFI report conceptual model indicated that Cañon de Valle alluvial sediment is a continuing secondary source for HE and barium (LANL 1998, 59891) that is capable of causing additional groundwater or soil contamination above regulatory standards. Sediment transport was identified as a key contaminant transport mechanism, and it was characterized as a dynamic process governed largely by the frequency and magnitude of runoff and flood events. The Phase III RFI provides additional data on the distributions and mobility of contaminated sediments in both Cañon de Valle and Martin Spring Canyon.

Geomorphic studies that were conducted as part of the Phase III RFI provide insight into the magnitude of the secondary source and the nature of sediment transport processes (Appendix E). An investigation into contaminants contained within the sediment deposits in Cañon de Valle and Martin Spring Canyon was conducted in 1999 and 2000. The investigation focused on characterizing the concentrations, distribution, and inventory of barium, HMX, and RDX in sediment deposits outside of the active channel. The work included geomorphic mapping and associated characterization of geomorphic units, as well as sediment analysis using field-screening and laboratory analyses. Estimates of the inventory of barium, HMX, and RDX in fine-grained sediment in the different intervals were made using data on the area, density, average thickness of fine-grained sediment, and average contaminant concentration in each unit.

A total of about 21,000 kg of barium is estimated to have been present in Cañon de Valle sediment before the Cerro Grande fire, roughly half of which would have been upstream from MDA P and half of which would have been downstream. About 62% is estimated to have been stored in fine-grained sediment deposits outside the active channel, about 10% is estimated to have been in the active channel, and the remainder would have been in coarse-grained deposits in abandoned channel units. This indicates that flood events play a key role in mobilizing contaminated sediments in and along the channel. Post-fire sediment sampling results show a decrease in active channel sediment concentrations and indicate a substantial downstream redistribution of barium due to post-fire flooding.

Estimates of the total inventory of HMX and RDX in Cañon de Valle sediment before the Cerro Grande fire indicate that approximately 50 kg of HMX was present, 50% of which occurred in fine-grained sediment and 50% of which occurred in coarse-grained sediment. Approximately 5 kg of RDX is estimated to have been present, of which about 60% was found in fine-grained sediment. Post-fire data showed generally lower RDX and HMX concentrations after the fire, indicating a substantial redistribution due to post-fire flooding.

Barium and RDX are both present in Martin Spring Canyon, but at much lower concentrations and with much smaller inventories than in Cañon de Valle. The estimated barium and RDX inventories in Martin Spring Canyon are approximately 820 kg and 0.2 kg, respectively. The source for RDX is groundwater discharge from Martin Spring, and the RDX probably first became adsorbed to organic matter and associated sediment in the stream bed. Subsequently, the sediment was suspended by scour during floods and redeposited on adjacent abandoned channels and floodplains.

In both Cañon de Valle and Martin Spring Canyon, the contaminant mass estimate is limited by the depth of the geomorphic sampling (maximum of 2 ft bgs). While the boring sampling results from the alluvial wells drilled during the Phase II and Phase III RFIs indicate minimal contamination at depth in the saturated alluvial/tuff contact, the vertical distribution of contaminants in the overlying saturated and unsaturated alluvial sediments is unknown.

# **5.2.4 Component 4—Springs in Cañon de Valle and Martin Spring Canyon**

Springs in Cañon de Valle and Martin Spring Canyon are labeled component 4 on Figure 5.1-1. The Phase II RFI detected HE, barium, and other contaminants in SWSC, Burning Ground, and Martin Springs (LANL 1998, 59891). The following key hypotheses from the Phase II RFI concern the conceptual model of the springs:

- the saturated systems that feed the springs may represent the discharge points of surge beds and fracture sets within the mesa;
- the springs are all located near the Unit 3/Unit 4 contact within the Tshirege Unit of the Bandelier Tuff, which is a zone characterized by several surge beds;
- the bromide tracer study demonstrates direct connectivity between the 260 outfall and SWSC Spring (and likely Burning Ground Spring);
- the springs have multiple sources for groundwater recharge; and
- the contaminants in Martin Spring may have come from a source other than the 260 outfall.

Martin Spring's flow and chemistry are substantially different from the two Cañon de Valle springs that were investigated. The Phase III RFI information improves the understanding of the hydrology and contaminant dynamics of the springs.

A substantial amount of monitoring data (e.g., flow, contaminant concentrations, stable isotopes, and temperature) have been collected at SWSC, Burning Ground, and Martin Springs since the 1998 Phase II RFI was completed. In addition, isotopic studies were conducted to better understand the hydrology of the springs. Details of the monitoring and isotopic studies are provided in various subsections within section 4.0 of this report. The following major physical changes have influenced the spring systems since the 1998 Phase II RFI conceptual model was developed: (1) the continuing multi-year drought; (2) the removal of contaminant inventories from the 260 outfall area, MDA P, and MDA R (discussed in section 5.2.1); and (3) the Cerro Grande fire in 2000 and forest thinning on the TA-16 mesa.

Isotopic studies of the spring flow systems (see section 4.4.2.1.7) show that the springs have two main modes of recharge. These modes can be described as (1) short-residence-time pathways which are driven by individual rain or snowmelt events; and (2) slower, long-residence-time pathways which provide base flow to the springs and where flows are controlled more by longer-term climatic variations. The drought has lessened the frequency of the short-residence-time recharge events, thus the contaminant concentrations observed during the drought are probably being transported via the slower long-residence base flow pathways. The stable isotope data indicate that base flow is largely recharged to the west, at elevations above TA-16 (and above any HE or barium contamination). Effects of the drought are substantial in that the discharge to all the springs has decreased and, for Martin Spring and SWSC Spring, flow has stopped completely.

This reduction in flow does not appear to have lowered the total mass flow rate of contaminants being released into Cañon de Valle and Martin Spring Canyon from the springs. Barium in Burning Ground Spring is an exception, with a weak, but statistically significant, decrease in mass flow rate (see Figures 4.5-2a through c). Therefore, base flow must be encountering a source of contamination in the mesa vadose zone as it travels to the springs. This would explain why there is no substantial decrease in contaminant mass in the spring discharges despite the reduction in short-residence-time pathway recharge. The lack of a reduction in mass, with a concurrent reduction of short-residence-time flow pathway recharge, indicates that the short-residence-time flow pathways may act to dilute contaminant

concentrations during heavier spring runoff events. This kind of behavior appears to be important at Martin Spring; however, it does not appear to be true for the Burning Ground and SWSC Springs. Instead, during high flow events, there appears to be a flushing effect in which contaminant mass increases during the period of high discharge, implying that additional subsurface contaminated zones are being encountered.

The effect of the drought on flow is probably also reducing or preventing the transport of some contaminants to the springs because little to no flow is taking place through formerly wet, now dry contaminated zones. This is the case at SWSC Spring, which is currently dry. Reduced accessibility to contaminants is supported by the bromide tracer study (see section 2.0) which showed that, after 3 years, much of the bromide tracer mass was still located within a few ft of where the tracer had been applied.

One of the justifications for the IM removal of contaminated materials from the TA-16-260 source area was that it would, over time, lower the concentrations of contaminants entering the Cañon de Valle springs. Analyses of contaminant time-series data since the IM was completed do not show any significant reduction in concentrations (with the exception of barium in Burning Ground Spring; see section 4.4). This lack of reduction is not a reflection of the overall long-term effectiveness of the source area IM; rather, it is likely due to three factors: (1) the drought, (2) deeper vadose zone contamination and related inventory, and (3) the long-residence-time component of spring flow. The drought has limited the transport of contaminants from shallow depths at the TA-16-260 source area. Thus, there has not been enough water flow to flush out the existing contaminants. There is current contamination in the vadose zone below the depths from which soil was removed during the IM, and this deeper contamination zone is what currently supplies the spring systems. The last factor that accounts for the lack of changes in spring contaminant concentrations is that the analysis of trends in spring flow shows a long-residence-time (base flow) component to spring discharge on the order of several years (section 4.4.2.1.9).

As noted earlier, the 2000 Cerro Grande fire and current forest thinning may alter the runoff/recharge relations on the mesa. Some studies show an increase in runoff in burned areas because of the loss of vegetative cover. If runoff increases, recharge to the springs could decrease thereby decreasing vadose zone transport of some contaminants. However, it is not known if this potential runoff/recharge shift would prove to be a substantial influence over the long term. The effect of tree thinning is less apparent. Removal of vegetation can increase runoff (similar to the potential fire effect), resulting in decreased recharge. However, removal of the Ponderosa pines will decrease transpiration losses of water, which could increase recharge. Current research studies of the effect of tree removal on recharge show a great degree of variability, and it is not clear what the long-term effect of tree removal will be on spring recharge at TA-16 (Wilcox 2002, 76860).

The Cerro Grande fire did alter the chemistry of the springs, although this appears to have been a shortterm perturbation. Spring monitoring showed increases in ions such as bicarbonate and calcium a few months after the fire. Monitoring of other springs on the Pajarito Plateau showed similar short-term changes in chemistry (Longmire 2001, 76889). It does not appear, however, that the fire strongly altered the concentrations of the main COPCs (i.e., RDX and barium). One of the primary effects on the concentrations of contaminants in the springs is the size of precipitation/recharge events. Although not all events or chemicals behave consistently (partly because of the distribution of recharge flow paths discussed earlier), there is strong evidence that—for some events—contaminant concentrations are temporarily lowered as a result of dilution (see section 4.0).

## **5.2.5 Components 5 and 6—Surface Water and Alluvial Groundwater in Cañon de Valle and Martin Spring Canyon**

Cañon de Valle and Martin Spring Canyon surface water and alluvial groundwater are important components of the conceptual model (Figure 5.1-1). Both represent potential human and ecological exposure sources, and both are critical in the overall site hydrogeological regime, which includes the regional aquifer. The principal physical features of Cañon de Valle are shown in Figure 5.2-1.

The Phase II RFI investigations identified the presence of RDX (maximum concentration of 818 µg/L), barium (99–16,000 µg/L), and lesser concentrations of other contaminants, in surface waters and alluvial groundwaters in Cañon de Valle (LANL 1998, 59891). Some key aspects of the conceptual model are

- surface runoff and spring flow contribute contaminants to the alluvial system, but the springs generally dilute the higher levels of contamination in the surface water and alluvial groundwater,
- alluvial groundwater disappears downgradient from MDA P and therefore there may be loss of water to underlying units, and
- there appears to be contaminant mixing between alluvial groundwater and surface water (during ephemeral flow) downgradient from MDA P.

The Phase III RFI results greatly improve the understanding of the surface water and alluvial groundwater system.

The alluvial groundwater and surface water systems include the alluvial and streamflow systems in Cañon de Valle and Martin Spring Canyon. Since the 1998 Phase II RFI, a substantial amount of flow and contaminant data have been collected in both canyons. These data include periodic discharge measurements of streamflow, alluvial groundwater water-level monitoring, contaminant sampling, and other monitoring data such as temperature and conductivity. The major changes to the system since the 1998 conceptual model was developed are the same as those described in sections 5.2.1, 5.2.2, and 5.2.4 for the TA-16-260 source area, the mesa vadose zone, and the springs (i.e., the IM source removal, the drought, the Cerro Grande fire, and subsequent tree thinning). This section focuses on refining the understanding of the alluvial groundwater and surface water systems by analyzing the new monitoring data.

An important feature incorporated into the conceptual model is based on the observation that the Cañon de Valle alluvium, and its associated groundwater, terminates or pinches out approximately 7000 ft east of the 260 outfall. The Cañon de Valle saturated alluvium may be viewed as a fixed volume with inputs (springs, precipitation, and groundwater flow) and outputs (evapotranspiration and leakage into the underlying fractured tuff that lessens water volume). A conceptual water balance model is shown in Figure 5.2-2, in terms of gal. per ft of canyon per day. As detailed in Appendix N, component flows were prepared using historical data for spring water flow, groundwater elevation in wells, historical averages for precipitation and evapotranspiration, and literature values for alluvial permeability in the absence of actual data. Based on these component flows, the rate of infiltration was estimated.

Assuming a steady state, the rate of loss of contaminated groundwater to the underlying tuff is estimated to be approximately 2.6 gal. per day per ft of canyon. Under the assumptions of this water balance model, springs and precipitation comprise the majority of input flow into the control volume, with groundwater flow into the control volume comprising less than 1%.







**Figure 5.2-2. Conceptual water balance model for the Cañon de Valle alluvial system, with calculated inputs and outputs in terms of gal. per ft of canyon per day** 

In terms of water balance, the springs contribute substantial amounts of water to the canyon bottom; exchange also occurs between the surface water and alluvial groundwater. These conditions affect contaminant distributions in the canyon bottom. Figure 5.2-3 presents examples of the effect of the springs, alluvial groundwater, and surface water interconnection on barium and RDX concentrations. Barium concentrations remain relatively consistent among the three types of water over low, medium, and high surface flow sampling events (see section 3.0), probably due to buffering by barium-contaminated sediments. Alluvial groundwater barium concentrations are the highest, surface water concentrations are intermediate, and the spring concentrations are the lowest. These results show that the spring water substantially dilutes the concentrations in the alluvial groundwater and surface water systems. The differences between the alluvial groundwater and surface water concentrations are largely controlled by the spatial distribution and buffering capacity of barium in the canyon sediment (section 3.0). For RDX, there is no consistency in contaminant concentrations. Spring water tends to have the lowest concentration and generally dilutes the alluvial groundwater and surface water.

Spatial trends of contaminants in surface water and alluvial groundwater, screening parameters, and flow provide other key insights into the alluvial system. Flow profiles indicate that there is a losing reach in the region between Burning Ground Spring and the area just upgradient from MDA P. In addition, temperature data, barium and RDX concentrations, and flow increases all indicate that alluvial groundwater may be discharging into the surface water system downgradient from Well 16-02659 (see Figure 5.2-1). The high RDX values in Well 16-02659 compared to upgradient Well 16-02658 indicate that either RDX is being leached from secondary sources within the alluvial system or that increased inputs into the alluvial groundwater system from higher concentration surface waters are occurring. In addition, the presence of both RDX and barium upgradient from the 260 outfall discharge point indicates that residual contamination at MDA R or the 90s Line Pond may also be a contributor to the alluvial system.



## **Figure 5-2-3. Comparison of barium and RDX concentrations in Cañon de Valle alluvial groundwater, springs, and surface water for selected flow events from 1998 to 2002**

Stable isotope results in the alluvial system indicate that the surface waters respond much more rapidly to precipitation events and other discharges to the surface, whereas alluvial waters represent more wellmixed waters that have had time to interact with alluvial sediments.

As part of Phase III RFI activities, a geophysical resistivity survey was conducted, the objectives of which included defining the lateral and vertical extents of saturated alluvium within Cañon de Valle along the survey lines and within the vicinity of established monitoring wells. A secondary goal was to investigate potential vertical pathways for downward migration of meteoric and groundwater into the Bandelier Tuff, which is discussed in section 5.2.6.

A longitudinal profile (roughly along the canyon axis) shows a series of shallow low-resistivity features occurring in the alluvium. These zones are possible areas of saturation or elevated water content, although the correlation between resistivity and water content has not been verified for TA-16. The discontinuous appearance of these zones probably relates to placement of the geophysical probes. Because of logistical difficulties, it was not possible to place the probes at the same distance from the stream channel; thus, the zones may be more continuous than they appear. Perpendicular profiles (across the canyon bottom) provide a better picture of the lateral extent of alluvial groundwater (assuming that resistivity and water content are negatively correlated). These profiles show two types of lowresistivity zones. The first type is associated with possible saturation or elevated water contents near the streambed. These profiles indicate that the alluvial aquifer probably does not extend across the width of the canyon; instead it is restricted to localized areas near the stream channel. The second type of lowresistivity zones relates to areas at, or adjacent to, the toe of the canyon walls. These areas indicate the possibility of interflow zones and/or seeps that contribute water to the canyon subsurface. The presence of these features is consistent with the temperature, flow, and geochemistry results discussed in section 3.0 which indicate alluvial recharge zones in the canyon, other than known springs.

Flowing surface water is present both perennially and intermittently within specific reaches of the Cañon de Valle channel. The approximate extent of perennial surface water is shown in Figure 5.2-1. Surface water occurs when either storm events produce precipitation rates that exceed the infiltration rate or the inflow of water into the alluvium exceeds the alluvial storage capacity. Both cases are heavily dependent on the configuration of the stream channel with respect to the surrounding bank slope and alluvium. For example, two locations along Cañon de Valle may have the same saturated alluvial thickness, but differing stream channel depths. For these cases, the deeper channel depth may contain flowing water while the other is dry. To maintain perennial flowing water, however, the local water balance of both systems must differ, given the more rapid rate of transport of flowing water in a perennial stream. In the conceptual water balance model presented in Figure 5.2-2, the stream transport term is not considered because the ends of the control volume are outside of the perennial reach.

Because the Cañon de Valle alluvial groundwater and surface water systems are interconnected and are the focus of risk assessment and possible remediation, investigations were conducted to characterize the geochemical conditions in the canyon bottom, particularly the redox (reducing or oxidizing) conditions in the alluvial groundwater (see section 3.4.2.2.4). The redox state of the alluvial groundwater can control the speciation and mobility of metals and the degradation of contaminants such as nitrate and the various HE compounds. The redox conditions focused on the alluvial groundwater because higher contaminant concentrations are generally present in the alluvial groundwater rather than in the surface water system, and lower flow rates allow more time for geochemical and biogeochemical reactions to occur. Redox conditions in the alluvial groundwater vary with time and distance along the canyon; this is consistent with a more detailed study of Jemez alluvial groundwater redox conditions done by Groffman and Crossey (1999, 76859). The presence of reducing conditions is important because nitrate and HE degradation occur under reducing conditions.

Analyses of nitrate concentrations and nitrogen stable isotopes (section 3.0) support the conclusion of active nitrate degradation in the canyon. Substantial amounts of barium nitrate were used at TA-16 and, although nitrate concentrations are elevated with respect to background levels, nitrate concentrations are likely not as high as would be possible in the absence of degradation. For the principal HE compounds (HMX, RDX, and TNT), there is also evidence of degradation products in the alluvial groundwater at TA-16.

Most of the data collected in the Phase III RFI indicate that the alluvial groundwater system in Cañon de Valle is heterogeneous in both contamination and hydrologic properties such as saturation. Contaminant concentrations in water do not represent a simple "plume" with decreasing concentrations from the source or center of the plume. Both RDX and barium increase and decrease in relative abundance in springs, surface waters, and alluvial groundwaters. This is due to variable exchange between surface and alluvial groundwaters dependent on the flow regime; variable degrees of mobilization of vadose zone and alluvial sediments; location of contaminant inventories; and varying degrees of dilution from runoff, interflow, and vadose zone discharge. Similarly, the geophysics, the piezometer results, and the results of head monitoring in the alluvial wells indicate that the saturated system in the Cañon de Valle alluvium is heterogeneous with respect to saturation and permeability.

## **5.2.6 Components 7 and 8—Deep Vadose Zone and Regional Aquifer**

The tuff underlying the canyons and the regional aquifer are labeled Components 7 and 8, respectively, in the conceptual model (Figure 5.1-1). The deep vadose zone and the regional aquifer were not extensively addressed in the Phase II RFI.

To better characterize the TA-16 deep vadose zone, two geophysical surveys were conducted (Appendix D; LANL 2003, 75986.2). The main objective of these surveys was to identify potential saturated zones deep in the mesa and the lateral extent of such zones. In 2001, an electromagnetic "flyover" survey was performed over the Laboratory. The survey data indicate a more conductive (presumably wetter, perhaps saturated) zone in the western half of the TA-16 mesa, ending in a steeply dipping zone of electrical conductivity in the vicinity of Regional Aquifer Well R-25. Regional Aquifer Wells CdV-R-37-2 and CdV-R-15-3 are located in the less conductive zone further to the east. These wells did not intercept the 700-ft-deep perched aquifer observed in Regional Aquifer Well R-25 (Kopp et al. 2003, 73707; Kopp et al. 2002, 73179.9). Zonge Engineering (Zonge) performed a controlled-source audio-frequency magneto-telluric (CSAMT) survey during 2002. The data indicate the presence of discrete heterogeneous, subvertical, electrically conductive layers (presumably wetter, perhaps saturated). The data also indicated a geophysical feature at Well R-25 which has been tentatively identified as the perched aquifer. Furthermore, based on the data, this feature (and inferred perched aquifer) may be limited to this location.

Based on the geophysical surveys, the intermediate-depth (approximately 700 ft) perched aquifer (and any associated contamination) below the TA-16 mesa is probably limited in extent. The Zonge data support the conceptual model hypothesis that vertical preferential pathways may be responsible for groundwater recharge and contaminant transport to perched groundwater zones (where present) and to the regional aquifer at Well R-25. Intermediate-depth wells scheduled for 2003 will provide further insights into vadose zone contamination and pathways.

During 1999, Well R-25 was drilled to a depth of 1942 ft from the mesa top above Cañon de Valle (see Figures 5.1-1 and 5.2-1) into the regional aquifer. Based on the groundwater elevation in this well, confined conditions may be present. HE contamination was detected in Well R-25 in 1999 and continues to be detected (at a maximum detected concentration of 75 µg/L) in ongoing quarterly samples (LANL 2003, 75986.2). Barium has not been detected. The lack of contamination in the regional aquifer at

Regional Aquifer Wells CdV-R-37-2 and CdV-R-15-3 (Kopp et al. 2003, 73707; Kopp et al. 2002, 73179.9), designed as plume-definition wells, also places bounds on the extent of contamination within the framework of the conceptual model. The locations of these wells are shown in Appendix B (Figure B-6). To assess the nature and extent of contamination, additional well installations are planned for the regional aquifer (Appendix B).

## **5.2.7 Other Potential Sources**

The main canyons and water catchments within TA-16 and the surrounding area consist of Cañon de Valle, Fishladder Canyon, and Martin Spring Canyon. Historical Laboratory operations have introduced contamination to these areas (LANL 1993, 20948). There are over 400 SWMUs identified within TA-16, and the SWMUs most likely to affect the area have been characterized (see section 1.2.3). Operations associated with these SWMUs overlap the water catchment boundaries, and it is difficult to accurately predict pathways from buildings or SWMUs to a particular spring or canyon.

## **5.2.8 Physical and Chemical Characteristics of the Contaminants and Environmental Fate**

One important part of the site conceptual model for hydrogeological and contaminant transport involves the chemical and physical properties of the contaminants and their behavior in the environment. Specific properties include the degree of saturation (barium minerals), the potential for ion exchange (barium) or sorption (TNT, HMX, or RDX on natural organic carbon), and the potential for natural bioremediation.

The high specific gravity of RDX and HMX indicates that particulates of these compounds were likely deposited near the 260 outfall and former settling pond, rather than carried into Cañon de Valle as particulates. Due to the lower specific gravity of TNT, this statement may not be true for TNT. The potential for particulate settling along the channel also depends on the flow velocity, flow rate, and residence time in the former settling pond—all factors which were not studied during the operational period of the outfall. The likely absence of particulate transport leaves the transport of dissolved constituents as the primary mechanism for transport of HE into Cañon de Valle. The solubility of RDX is approximately 60 mg/L at 25°C. The solubilities of TNT and HMX, as well as other properties of RDX, HMX, and TNT, are shown in Table 5.2-1.

In contrast to RDX, HMX, and TNT, which do not dissociate in groundwater, barium nitrate dissociates into the barium cation and nitrate anion, and is freely soluble in water. In the Cañon de Valle alluvium, barium exists in both dissolved and solid phases, the latter includes barite (BaSO<sub>4</sub>) and witherite (BaCO<sub>3</sub>) (LANL 1998, 59891). It is likely that both minerals represent a substantial portion of the total barium inventory. The two solid phase compounds differ, however, in solubility. Once precipitated, barite will remain insoluble under natural conditions. Witherite that is present in the alluvial sediment under dry conditions may dissolve under wet, more saturated conditions.

<b>Property</b>	<b>RDX</b> a	<b>HMX</b> <sup>a</sup>	<b>TNT</b>
<b>CAS</b> number	121-82-4	2691-41-0	$118 - 96 - 7^b$
Empirical formula	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_7H_5N_3O_6{}^b$
Molecular weight	222.15	296.2	$227.13^{b}$
Melting point (°C)	205	286	82 <sup>b</sup>
Density ( $g/cm3$ )	1.83	1.9	$1.65^b$
Water solubility (mg/L)	60 (25°C)	$5(25^{\circ}C)$	200 $(15^{\circ}C)^{b}$
Vapor pressure (torr)	$4.03 \times 10^{-9}$ (25°C)	$3.33 \times 10^{-14}$ (25°C)	$1.99 \times 10^{-4}$ (20°C) <sup>c</sup>
$K_H$ (atm-m <sup>3</sup> /mole, 25°C)	$1.96 \times 10^{-11}$	$2.60 \times 10^{-15}$	$4.57 \times 10^{-7}$
$Log K_{ow}$	0.87, 0.81, 0.86	0.26, 0.06	$2.25^{b}$
$Log K_{oc}$	2.00	0.54	$2.48^{b}$

**Table 5.2-1 Physical Properties of RDX, HMX, and TNT** 

a Card and Autenrieth 1998, 76873.

b Montgomery 1991, 76189.

c USDHHS 1995, 76187.

atm = atmospheres

CAS = chemical abstract service

K<sup>H</sup>= Henry's Law

 $K_{oc}$  organic carbon sorption coefficient

Kow= octanol-water partition coefficient

Log = logarithmic base 10

Dissolved HE in groundwater will partition between a soluble and a sorbed phase. Both tuff and sediment are present within the subsurface, and both will sorb HE, though to a varying extent. On the basis of RDX contaminant sorption studies done on clays (Myers 2003, 76188), it can be inferred that tuff has a relatively low sorption capacity (on the order of 1 mL/g) for RDX, HMX, and TNT. These constituents will be sorbed on organic carbon present in the Cañon de Valle alluvium, with the capacity for sorption represented by the compound-specific organic carbon sorption coefficient  $(K_{oc})$ . While the fraction organic carbon (FOC) in the alluvium is not known, FOC studies in Los Alamos Canyon (Hickmott 2003, 76190) indicate that FOC ranges from 0.1 to 5%. Finer fractions, like fine sand and silt, that are representative of floodplain deposits tend to be in the higher end of the FOC concentration range (e.g., 2–5%), while concentrations in the medium sand and larger fractions that are representative of buried channel deposits tend to be in the lower end of that range (e.g., 0.1–2%).

Barium has an affinity for adsorption on clays, oxides, and hydrous oxides, with literature values for equilibrium sorption coefficients in soil ranging from 66 to 2800 mL/g (Myers 2003, 76188). Although the concentrations of clays has not been studied in Cañon de Valle, clay content has been quantified for other canyons, and it generally correlates with the fine particle size fraction (Katzman 2003, 76850). For Cañon de Valle, the fine particle size fraction appears to contain the highest contaminant inventories compared to other geomorphic units, indicating that the clay content of the fine particle size fraction may be important (section 3.4.2.5.5). Barium sorption on these clay and oxide minerals takes the form of ion exchange and chemisorption, with sorption on clays primarily due to ion exchange. Furthermore, barium sorption on clay is thought to be irreversible under natural conditions. Once barium is sorbed, it is immobilized or "locked down" on the clay surface (Myers 2003, 76188). Consequently, ion exchange of barium on natural clay can serve as a means of immobilizing barium or retarding its movement in the environment.

A literature search for barium sorption studies on tuff was also conducted, but yielded no published studies. The dynamics of barium sorption on both tuff and alluvial sediment is an important gap in the conceptual model, especially with regard to its irreversibility and implications for the environmental fate of barium.

The physical and chemical properties of HE offer important insight into the environmental availability and fate of contaminants. Figure 5.2-4 shows the conceptual vadose zone distribution of barium and RDX, the two primary COPCs present in Cañon de Valle alluvial sediment. In Cañon de Valle, the alluvial water table fluctuates seasonally due to precipitation. Rising groundwater levels will dissolve barium minerals, primarily witherite, that are present in the unsaturated zone. Rising groundwater also causes the release of RDX-containing pore water previously trapped in the vadose zone. RDX and barium are also present as sorbed phases; barium is sorbed to clay particulates and other mineral phases; and RDX is sorbed to organic carbon present in the sediment. Alternatively, falling groundwater tables may cause the evaporation of water and the precipitation of barium minerals. In either scenario, the presence of these forms of barium and RDX in alluvial sediments represents a widespread continuing source that is mobilized by stormwater or a rising alluvial groundwater table associated with episodic precipitation events in Cañon de Valle.



Block of Cañon de Valle alluvium

#### **Figure 5.2-4. Conceptual distribution of RDX and barium in the Cañon de Valle vadose zone**

The relative sorption potential of barium and RDX is reflected in their respective contaminant distributions. In Regional Aquifer Well R-25, barium has not been detected, whereas RDX has been detected at a maximum concentration of 75 µg/L. This difference is likely related to the higher relative sorption potential for barium on tuff.

The potential for biodegradation is another chemical property that is important in the long-term environmental fate of HE. TNT degrades aerobically and anaerobically, with reduction of the nitroso groups, eventually leading to cleavage and assimilation or mineralization of a portion of the TNT carbon. Groundwater analytical data from Cañon de Valle indicate active TNT degradation, with breakdown products (i.e., amino-2,6-dinitrotoluene[4-] and amino-,6-dinitrotoluene [2-]) typically present in higher concentrations than TNT itself. One important drawback to aerobic degradation of HE is that significant amounts of the TNT carbon are left as refractory dead-end products of uncertain toxicity (Card and Autenrieth 1998, 76873). Anaerobic degradation rates are typically greater than aerobic rates. For either pathway, nutrient concentrations are also important. In subsurface regions of the conceptual model,

including the mesa vadose zone, canyon alluvium, and alluvial groundwater, the rate of natural biodegradation of RDX and HMX is likely to be low, given the lack of appropriate anaerobic conditions. RDX and HMX can also degrade chemically via an inorganic pH hydrolysis reaction (Layton et al. 1987, 14703). Groundwater and surface water at TA-16 typically have pH values high enough that hydrolysis may be important over the long term. However, the importance of this inorganic degradation pathway will require further assessment.

Barium does not biodegrade because it is an inorganic contaminant. In addition to the sorption of barium on naturally occurring tuff and clay minerals, barium forms a stable sulfate compound (barite) that is insoluble under natural conditions. Like sorption, the formation of barium sulfate serves as a natural form of stabilization for barium.

# **5.2.9 Conceptual Model Uncertainties**

Despite the refinements of the TA-16 conceptual model and general reinforcement of the 1998 conceptual model, uncertainties about the TA-16 system remain, as discussed below.

- 1. Characterization activities have not yet bounded the vertical extent of subsurface contamination beneath the potential source areas located on the mesa. Consequently, there is not enough information to accurately bound the mesa vadose zone contaminant inventories. Future drilling activities (e.g., at the 90s Line Pond) may help clarify these uncertainties.
- 2. The uncertainties about the hydrogeology of the springs include the effects of the termination of 260 outfall discharges and the drought. Also, it is not clear if and when the benefits of the IM source removal at the TA-16-260 source area will be evident at the Cañon de Valle springs.
- 3. As noted in the 1998 Phase II RFI report, there is little evidence for a hydrogeological link between the 260 outfall and Martin Spring. Additional characterization since 1998 reinforces the idea that the Martin Spring system is affected by contaminant sources other than the 260 outfall (see sections 4.4.2.1.1, 4.4.2.1.2, and 4.4.2.1.7). Other potential source areas exist, but these have not been positively identified as contributing contamination at Martin Spring. The planned additional mesa characterization through intermediate-depth borings should help clarify this uncertainty, as discussed in revision 1 to the CMS plan addendum (LANL 2003, 75986.2).
- 4. As discussed in section 5.2.6, the hydrogeological interconnection between the canyon bottoms and the deeper groundwater systems (including the deep perched aquifer encountered in Regional Aquifer Well R-25 and the regional aquifer) is not well characterized. The lateral extent of the 700-ft perched aquifer encountered in Regional Aquifer Well R-25 is not well bounded (although Regional Aquifer Wells CdV-R-15-3 and CdV-R-37-2 improved this). The Zonge geophysical survey (Appendix D) indicates there may be an abrupt eastern boundary to the deep perched aquifer, but this has not been verified. In addition, the connection between the perched aquifer and the regional aquifer is not well characterized. These uncertainties will be addressed by other planned investigations (LANL 2003, 75986.2). In particular, three intermediate-depth wells have been proposed: one within Cañon de Valle near Regional Aquifer Well R-25, one near the Burning Ground, and one near Building 340.
- 5. The character of the lateral distribution of contaminant concentrations within Cañon de Valle alluvium is not known. Of the estimated 7000 ft of suspected saturated alluvium downstream from the TA-16-260 source area, monitoring wells are located along first 4000 ft. In addition, no groundwater or sediment samples have been obtained within an area 2000 ft upstream from existing sample points located at the confluence of Cañon de Valle and Water Canyon. The RRES-RS Canyons team will sample the groundwater and sediment in these reaches as part of their investigations into the Water Canyon and Cañon de Valle watersheds.
- 6. The distribution of permeability in Cañon de Valle saturated alluvial sediment is not known. These data are important to refining the water balance and to assessing the efficacy of groundwater remediation alternatives, such as groundwater recovery, in the CMS.
- 7. Potential areas of enhanced vertical groundwater infiltration within the Cañon de Valle alluvium can be inferred from geophysics resistivity results. These areas include a reach to the west of MDA P. The permeability of the sediment or fractures that comprise these areas is not known. Moreover, the correlation between geophysics resistivity data and water content has not been verified by field sampling. Additional subsurface investigations, as planned under revision 1 to the CMS plan addendum (LANL 2003, 75986.2), will include the installation of intermediate-depth wells in Cañon de Valle to help verify the geophysical interpretations.

# **6.0 SUMMARY OF RISK ASSESSMENTS**

This section summarizes the results of the human health and ecological risk assessments completed for Cañon de Valle; the details can be found in Appendixes K and L, respectively.

## **6.1 Human Health Risk Assessment Summary**

For human health, baseline risk assessments were performed according to EPA guidance. Because the site is divided into two areas for investigation, two human health baseline risk assessments are included in this section. The baseline risk assessments for the source area and for the Cañon de Valle alluvial area are based on the investigation results described in sections 2.0 and 3.0, along with spring data from section 4.0.

## **6.1.1 Methodology**

Generally, the assessment process includes evaluation of data and identification of COPCs, development of source-term concentrations of COPCs, exposure assessment and quantification of COPC intake, evaluation of COPC toxicity, and characterization of potential risk. Each of these steps in the assessment process is described further in this section. A screening analysis was performed to identify the COPCs requiring further evaluation in a baseline analysis.

# **6.1.1.1 Data Evaluation and Identification of COPCs**

The COPCs retained for evaluation in the risk assessment were identified using data from the source area and Cañon de Valle alluvial area investigations as described in sections 2.0, 3.0, and 4.0 of this report.

# **(a) Source Area**

The results of the initial surface soil and tuff data review are presented in section 2.0 of this report. Detected chemicals were excluded from the analysis if any one of the following statements was true: (1) the chemical is an essential nutrient, (2) the detected concentrations occur in fewer than 5% of samples analyzed (if 21 or more samples are analyzed), or (3) measured concentrations are equal to or less than the Laboratory-wide background concentrations (LANL 1998, 59730).

The detected chemicals in soil and tuff that were not excluded were then compared with site-specific riskbased SALs under residential scenarios.

The chemicals that were detected above SALs in at least one sample were identified as COPCs for the source area risk assessment. The following chemicals were retained as COPCs for the baseline risk assessment: aluminum, arsenic, barium, manganese, thallium, uranium, HMX, RDX, and TNT.

# **(b) Cañon de Valle Alluvial Area**

The results of the initial sediment, surface water, and springs data review for the Cañon de Valle alluvial area are presented in section 3.0 (sediment and surface water) and section 4.0 (springs), for post-1998 analytical data only. The pre-1998 analytical results for the Cañon de Valle alluvial area were summarized in the Phase II RFI report (LANL 1998, 59891) and are provided in Appendix G-4 to this report. Surface water and springs data were evaluated as a single medium, based on their similar potential exposure, and are referred to as surface water for the remainder of this section.

Detected chemicals were excluded from further consideration if any one of the following statements was true: (1) the chemical is an essential nutrient, (2) the chemical is detected in fewer than 5% of samples analyzed (if 21 or more samples are analyzed), or (3) the concentration is equal to or less than the Laboratory-wide sediment background concentrations.

The detected chemicals in sediment that were not excluded were then compared with SALs. Chemicals in sediment that were detected above SALs in at least one sample were identified as COPCs for the Cañon de Valle alluvial area risk assessment. The following chemicals were retained as COPCs for the Cañon de Valle alluvial area baseline risk assessment: aluminum, antimony, arsenic, barium, chromium, lead, manganese, silver, thallium, uranium, benzo(a)pyrene, dinitrobenzene[1,3-], hexachlorobenzene, indeno(1,2,3-cd)pyrene, nitrobenzene, RDX, and TNT.

Those detected chemicals in surface water that were not excluded were further screened against the NMWQCC regulations numeric standard and the EPA MCL for drinking water. If both the NMWQCC regulations numeric standard and the EPA MCL were available, the more conservative standard (the lower concentration) was chosen for comparative screening purposes. In the absence of both an NMWQCC regulations numeric standard and an EPA MCL, the corresponding EPA Region 6 or Region 9 tap water PRG was selected.

The following chemicals were retained as COPCs for surface water in the Cañon de Valle alluvial area baseline risk assessment: aluminum, antimony, arsenic, barium, cadmium, cesium, chromium, cyanide, lead, manganese, mercury, rubidium, selenium, silver, thallium, uranium, amino-2,6-dinitrotoluene[4-], amino-4,6-dinitrotoluene[2-], bis(2-ethylhexyl)phthalate, bromomethane, chloromethane, dichloroethane[1,2-], dinitrobenzene[1,3-], dinitrotoluene[2,6-], dinitrosodimethylamine (DNX), methylene chloride, mononitrosodimethylamine (MNX), nitrate-nitrite as N (evaluated as nitrite), nitrobenzene, nitrotoluene[3-], nitrotoluene[4-], perchlorate, RDX, TNT, americium-241, and ruthenium-106. Of the COPCs listed above, the following were retained as COPCs only in the Phase II RFI: chromium, bromomethane, chloromethane, dichloroethane[1,2-], dinitrobenzene[1,3-], dinitrotoluene[2,6-], methylene chloride, nitrotoluene[3-], nitrotoluene[4-], americium-241, and ruthenium-106.

# **6.1.1.2 Development of Source-Term Concentrations**

A representative exposure concentration was calculated for each COPC because of the uncertainty associated with characterizing chemical concentrations in affected environmental media. This representative concentration is the source term used for the assessment of exposure to human receptors. Guidance provided by the EPA (1989, 08021) and LANL (2000, 66801) for exposure assessments describes the evaluation of a central tendency estimate (CTE) scenario and a reasonable maximum exposure (RME) scenario for each receptor. The EPA recommends using the mean concentration for the CTE assessment, and an estimate of the upper confidence limit (UCL) on the mean, or an appropriately similar measure, as the source term concentration for an RME assessment (EPA 1989, 08021).

Statistical tests were performed on the data describing the concentrations of each COPC identified for soil, tuff, sediment, and surface water to ensure that the assumptions inherent in the UCL calculations are valid. The EPA program ProUCL (Lockheed Martin 2002, 73767) was used to determine data distributions. If the concentrations of a chemical have a normal distribution, the 95% UCL was calculated using the Student's *t*-statistic. If the data are not normally distributed, the 95% UCL was calculated using the nonparametric bootstrap method (for both lognormal and nonparametric distributions). More details regarding the statistical analyses can be found in Appendix I-1. The mean and 95% UCL concentrations of COPCs that were used as source terms for the risk assessments of the source area and Cañon de Valle alluvial area are provided in Appendix K (Tables K-5 and K-6).

# **6.1.1.3 Exposure Assessment**

As done in the Phase II RFI report (LANL 1998, 59891), the baseline risk assessment for the source area includes potential exposures of an on-site environmental worker, a trail user, and a construction worker, and it incorporates the assumptions of that report. These are the most likely current and proposed future receptors in the source area. For the alluvial area, the baseline risk assessment is limited to potential exposure of a trail user. No groundwater from the site is available for drinking water use, and potential exposure to groundwater will be evaluated in the regional groundwater CMS.

# **(a) Source Area**

The conceptual site model (CSM) of the source area indicates the complete pathways identified for potential worker exposures (Appendix K). Soil/tuff residues can be released into the air by airborne dust suspension and volatilization from soil. Receptors could come into direct contact with COPC residues in soil/tuff and be exposed by incidental ingestion of soil/tuff or by dermal contact with soil/tuff. No bodies of surface water exist in the source area; therefore, there is no complete pathway for direct contact with surface water or sediment. No groundwater from the site is available for drinking water use, and potential exposure to groundwater will be evaluated in the regional groundwater CMS. The following complete exposure pathways were quantitatively evaluated in the risk assessment for the source area (Appendix K):

- inhalation of volatiles or dust particles from soil/tuff,
- incidental ingestion of soil/tuff, and
- dermal contact with soil/tuff.

The pathways described above are the most likely ones for receptors based on the activities that take place at the source area (LANL 1998, 59891; LANL 2000, 64355.4). The on-site environmental worker represents individuals involved in environmental monitoring such as field-sampling. The trail user is a worker who uses the trails for recreation/exercise purposes such as walking or jogging. The construction worker represents individuals involved in more intrusive work activities such as excavation. All human receptors evaluated according to these scenarios are assumed to have the same complete exposure pathways (Appendix K) but different work patterns, patterns which affect the frequency and duration of exposure.

#### **(b) Cañon de Valle Alluvial Area**

The CSM for the alluvial area (Appendix K) indicates the complete pathways identified for potential human exposure. Because bodies of surface water do exist in the Cañon de Valle alluvial area, there are complete exposure pathways for direct contact (ingestion and dermal) with sediment and, to a lesser extent, surface water. For surface water, direct contact is expected to be minimal. Trail users are not expected to be in direct contact with the surface water (i.e., wading) under normal conditions, and the use of the surface water as a potential drinking water source is even more unlikely. However, both of these pathways were evaluated within this risk assessment. In addition, inhalation of dust is considered to be a minor pathway for the alluvial area due to the limited exposed soil or sediment within the canyon (i.e., the alluvial area is well vegetated and/or wet). No groundwater from the site is available for drinking water use. Therefore, ingestion and dermal contact pathways for exposure to groundwater are incomplete at the alluvial area and are not evaluated in this risk assessment. However, potential exposure to groundwater will be evaluated in the regional groundwater CMS.

The following complete exposure pathways were quantitatively evaluated in the risk assessment for the alluvial area (Appendix K):

- incidental ingestion of sediment and surface water,
- dermal contact with sediment and surface water, and
- inhalation of fugitive dust.

The only potential receptor for the alluvial area is a trail user; a trail user is defined as a worker who uses the trails for recreation/exercise purposes such as walking or jogging and who may access the canyon for this purpose. Currently this is the only potential receptor for the alluvial area, and the future land use is expected to remain recreational (i.e., a worker who uses trails for recreation/exercise purposes).

## **6.1.1.4 Quantification of Chemical Intake**

EPA guidance and LANL guidance (EPA 1989, 08021; LANL 2000, 66801) provide the methods for estimating the pathway-specific exposures using exposure parameters that are appropriate for each complete pathway.

Intake doses were calculated using the following generic equation:

Chronic Daily Intake (LADD or ADD) = 
$$
\frac{C \times CR \times EF \times ED}{BW \times AT_{(c \text{ or } nc) } \times 365 \text{ days/yr}}
$$

where:



The contact rate refers to the amount of contaminated medium contacted per unit of time or event and it can be comprised of several parameters. The contact rate for the soil ingestion pathway, for example, is the amount of contaminated soil that an individual ingests during a specific time period.

The methodology and the receptor-specific exposure parameter assumptions for each complete exposure pathway evaluated are provided in LANL (2000, 66801) and are summarized in Appendix K. The receptor-specific exposure parameters are provided in Table K-7.

# **6.1.1.5 Toxicity Evaluation**

Toxicity assessment is the process of using the existing toxicity information from human or animal studies to identify potential health risks at various exposure levels in exposure populations (EPA 1989, 08021). The relationship between the exposure to a chemical, which is expressed as CDI, and an adverse health effect, which is expressed as a toxic response to a specific intake, must be quantified in order to assess potential health risks.

The methods used to develop toxicity factors differ depending on whether the COPC is a potential carcinogen or causes noncancer health effects. The most recently available toxicity factors developed by regulatory agencies and other sources were used, based on the following hierarchy of sources:

- 1. EPA's Integrated Risk Information System (www.epa.gov/iris)
- 2. EPA's Health Effects Assessment Summary Tables (EPA 1997, 58698)
- 3. Other primary literature sources cited in context

Oral toxicity values (both slope factors and references doses) were used for the quantitative evaluation of dermal exposure (EPA 2002, 76867).

#### **6.1.1.6 Risk Characterization**

Risk characterization integrates the COPC selection, exposure assessment, and toxicity assessment to describe the risks of potential adverse health effects to human receptors according to the assumed exposure scenarios. Because the causes of cancer and noncancer effects are assumed to result from different mechanisms of action, the evaluation of carcinogenic and noncarcinogenic effects use different methodologies.

The NMED soil screening levels (SSLs) are generally based on a  $10^{-5}$  target risk for carcinogens, or a hazard quotient (HQ) of 1 for noncarcinogens (NMED 2000, 68554). In addition, EPA (NCP 1990, 76875) defines a maximum acceptable range of incremental lifetime cancer risk (ILCR) as  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  or a maximum HQ of 1.0 for the purposes of recommending further action at a site.

#### **6.1.2 Human Health Risk Assessment Results**

This section summarizes the results of the human health risk assessments for both the source area and Cañon de Valle alluvial area. The potential risks calculated for each receptor, COPC, and pathway are detailed in Appendix K.

# **6.1.2.1 Source Area**

The cumulative excess cancer risk to all human receptors from potential exposures to COPCs in soil and tuff are within or below the  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  range of acceptable risk specified by EPA (1991, 56140) under both CTE and RME assumptions. In addition, the cumulative excess cancer risk to all human receptors, except the environmental worker receptor (estimated according to the RME assumptions), was equivalent to, or less than, the NMED target risk level of  $1 \times 10^{-5}$ . Cancer risks ranged from  $9 \times 10^{-7}$ (environmental worker) to  $4 \times 10^{-7}$  (trail user) for the CTE assumptions, and from  $3 \times 10^{-5}$  (environmental worker) to 3×10<sup>-6</sup> (trail user) for the RME assumptions. Risks associated with potential inhalation of fugitive dust are negligible compared to those associated with the ingestion and dermal contact pathways (see Tables K-12a, K-16a, and K-20a in Appendix K).

The cancer risk associated with exposure to RDX is the greatest contributor to the cumulative cancer risk estimates of RME exposures for the environmental worker, the trail user, and the construction worker. Arsenic and TNT also contribute to the cumulative cancer estimates by both the ingestion and dermal pathways for all three types of receptors.

The noncancer hazard estimates that were made according to CTE assumptions are below the acceptable HI of 1.0 specified by the NMED (2000, 68554) and EPA (NCP 1990, 76875) for the environmental worker, the trail user, and the construction worker. According to RME assumptions, the only receptor above the acceptable HI of 1.0 was the construction worker  $(HI = 2.0)$  (see Tables K-12b, K-16b, and K-20b in Appendix K).

The noncancer hazards associated with the exposure to TNT, RDX, and barium are the greatest contributors to the cumulative hazard estimates of RME exposures for the environmental worker, the trail user, and the construction worker. However, the individual COPC HQs did not exceed 1.0 for any of the receptors under either CTE or RME assumptions.

In summary, the cumulative excess cancer risk to all human receptors from potential exposures to all COPCs in soil and tuff was slightly above, or less than, the  $10^{-5}$  target risk specified by the NMED (2000, 68554) under either CTE or RME assumptions. Noncancer hazards are below an HI of 1.0 for CTE exposure assumptions, and below, or slightly above, an HI of 1.0 for RME assumptions (the maximum HI is 2.0 for the RME construction worker).

# **6.1.2.2 Cañon de Valle**

The cumulative excess cancer risk from potential exposures to COPCs in sediment and surface water are below the 1×10<sup>-5</sup> target risk specified by the NMED (2000, 68554) under both CTE (mean COPC concentration) and RME (95% UCL concentration) assumptions for all of the pathways evaluated. In addition, the cumulative excess cancer risks were all below the NMED target risk level of  $1 \times 10^{-5}$ .

The cancer risk associated with exposure to RDX is the greatest contributor to the cumulative cancer risk estimates for exposure in both sediment and surface water. Arsenic and benzo(a)pyrene contribute appreciably to the cumulative cancer estimate for exposure to sediment (see Table K-25a in Appendix K).

The noncancer hazard estimates made according to CTE and RME assumptions are below the acceptable HI of 1.0 specified by the NMED (2000, 68554) for the trail user and all exposure pathways (see Table K-25b in Appendix K).

In summary, the cumulative excess cancer risk to the trail user from potential exposures to all COPCs in sediment and surface water is below the  $1 \times 10^{-5}$  target risk specified by the NMED (2000, 68554) Noncancer hazards are also below the HI of 1.0 for both exposure assumptions.

# **6.1.2.3 Martin Spring Canyon**

For Martin Spring Canyon, a COPC concentration comparison was done between relative COPC concentrations (maximum and mean) in sediment and surface water and those found at the Cañon de Valle alluvial area. It was concluded that the Martin Spring Canyon COPC concentrations were less than, or within the range of, those found at the Cañon de Valle alluvial area, and therefore the concentrations in Martin Spring Canyon do not pose a potential unacceptable risk to human receptors under the trail-user scenario.

Nine of the chemicals retained as COPCs in sediment for Cañon de Valle were not retained as COPCs in sediment for Martin Spring Canyon. The only COPC in sediment that had a Martin Spring Canyon maximum concentration greater than its Cañon de Valle alluvial area counterpart was arsenic (10 mg/kg versus 4.2 mg/kg). The ILCR for arsenic in sediment in the Cañon de Valle alluvial area baseline risk assessment for the RME scenario was 3E-07; the arsenic concentration in sediment at Martin Spring Canyon does not substantially increase the risk of 3E-07 calculated for the Cañon de Valle alluvial area. A comparison between the mean and the 95% UCL of the mean for sediment concentrations shows similar results (see Table 4 in Appendix K).

Seventeen of the chemicals retained as COPCs in surface water at Cañon de Valle were not retained as COPCs in surface water at Martin Spring Canyon. The only COPCs in surface water that had a Martin Spring Canyon maximum concentration greater than their Cañon de Valle alluvial area counterparts were arsenic (75.1 µg/L versus 27 µg/L), manganese (67,800 µg/L versus 2200 µg/L), mercury (1.1 µg/L versus 1 µg/L), nitrate/nitrite (3,800,000 µg/L versus 3,380,000 µg/L), nitrobenzene (100 µg/L versus 50 µg/L), and selenium (38.3 µg/L versus 10 µg/L). None of these surface water COPCs were risk drivers in the baseline risk assessment for Cañon de Valle alluvial area; based on the similarity of the concentrations (all are less than, or equal to, one order of magnitude, with the exception of manganese), the risk from exposure to surface water at Martin Spring Canyon is similar to, or less than, that at Cañon de Valle. A comparison of mean surface water concentrations shows similar results (see Table K1-5 in Appendix K)**.**

## **6.1.3 Uncertainty Analysis**

Consideration of the uncertainty associated with the risk assessment process provides additional information for an informed interpretation of the results and allows better risk management decisions.

Uncertainties in final risk estimates from a baseline risk assessment may result from both the use of assumptions or models in lieu of measured data and from errors inherent in the estimation of exposure parameters. These uncertainties may result in the potential over- or underestimation of receptor-specific risks. Generally, the primary sources of uncertainty are associated with (1) environmental sampling and analysis and the selection of COPCs, (2) exposure assessment, and (3) toxicity assessment.

## **6.1.3.1 Environmental Sampling and Analysis and COPC Identification**

Errors in chemical analyses may come from several sources, including errors inherent in the sampling and analytical procedures. Errors in analytical accuracy or sampling can result in the qualification of data, which increases the uncertainty in source-term concentrations. Data that contained serious errors and could not be appropriately qualified for use in the risk assessment were rejected to reduce error.

A primary uncertainty associated with the COPC identification process is the possibility that a chemical may be inappropriately identified or eliminated as a COPC. It is unlikely that inorganic chemicals were inappropriately excluded because the only detected inorganic chemicals excluded were those determined to be no different than background levels. Arsenic was a significant contributor to the carcinogenic risk at both the source area (in soil and tuff) and at the Cañon de Valle alluvial area (for sediment). However, the arsenic 95% UCL concentrations are within the range of the Laboratory-wide background levels for all three media (LANL 1998, 59703), indicating that potential exposure to arsenic at either the source area or the Cañon de Valle alluvial area is similar to background levels and that the carcinogenic risk due to potential exposure to arsenic would not be different from background. The COPC selection process used in this risk analysis has resulted in an overestimation of risk, based on the screening scenario evaluated (residential). All detected chemicals were initially considered to be COPCs, even in cases where the frequency of detection was less than 5% for both inorganic and organic COPCs. The chemicals detected in less than 5% of the samples were retained as COPCs if the maximum detection or detection limit of the analysis exceeded the SAL. For example, benzo(a)pyrene was detected in one of 43 sediment samples for the Cañon de Valle alluvial area, but it was retained as a COPC due to high detection limits.

#### **6.1.3.2 Exposure Assessment**

Exposure assessment incorporates assumptions regarding the use of a site and the activities of receptors using the site. Because the activities of receptors at the site are variable and unpredictable, assumptions

and inferences were made to include these uncertainties in overestimated exposures. These elevated exposure estimates lead to conservative estimates of risk.

Sources of uncertainty in exposure assessments include the uncertainties in (1) exposure point concentration estimates, (2) time and duration of exposure, and (3) chemical intake calculation. Variability or heterogeneity in exposure routes and exposure dynamics such as age, gender, behavior, genetic constitution, state of health, and random movement of the potentially exposed populations also introduces uncertainty into the exposure estimates. Assessing exposures according to CTE and RME assumptions is one method for estimating the impact of these uncertainties on the range of estimated risks.

Assuming that the concentration in bulk soil, sediment, and surface water is the same as the exposurepoint concentration introduces uncertainty into the exposure analysis. Environmental sampling at the source area was designed to assess the soil after the IM of the area most affected by the outfall. The exposure-point concentrations are reasonable estimates of exposure. For the Cañon de Valle alluvial area, the sampling focused on the entire reach of the canyon and, to some extent, the discharge point of the springs. Therefore, the mean and UCL concentrations are reasonable estimates of potential exposure-point concentrations for the Cañon de Valle alluvial area.

Because all the chemical concentrations measured in soil, sediment, and surface water were assumed to be constant over the exposure period, the estimated exposure doses are probably overestimated. In addition, a large portion of the HE source has been removed from the source area, and the potential transport to the Cañon de Valle alluvial area is expected to decrease over time. Therefore, the use of all available historic data for the Cañon de Valle alluvial area will result in an overestimation of exposurepoint concentrations.

The goal of characterizing the time of contact is to develop estimates of contact frequency and duration of exposure. For this risk assessment, the exposure values were taken from LANL (2000, 66801), the Phase II RFI report (LANL 2000, 59891), and the IM report (LANL 2002, 73706). However, in the absence of site-specific data, the exposure assumptions used were consistent with EPA-approved parameters and default values (EPA 2002, 76867). When several upper-bound values are combined (e.g., as in the RME scenario) to estimate exposure for any one pathway, the resulting risk can exceed the  $99<sup>th</sup>$  percentile of the "expected risk" and therefore, may overestimate the range of risk that may be reasonably expected. Values developed for CTE and RME assumptions were used for all scenarios evaluated. By evaluating both the CTE and RME scenarios, a bounding of the potential risk is determined (i.e., a measure of the reasonable maximum risk versus the central tendency risk). The real risks at the source area and the Cañon de Valle alluvial area are expected to be somewhere in between these measures; thus, the risks are bounded for each potential receptor.

# **6.1.3.3 Toxicity Assessment**

EPA toxicity values [reference doses (RfDs) and slope factors (SFs)] were used to derive the nonradiological SALs used in this risk screening assessment and in the calculation of baseline risks (EPA 2001, 70109; EPA 1997, 58968). Uncertainties were identified in four areas with respect to the toxicity values: extrapolation from animals to humans, extrapolation from one route of exposure to another route of exposure, individual variability in the human population, and use of a surrogate to estimate toxicity.

1. *Extrapolation from animals to humans*—The SFs and RfDs are often determined by extrapolating from animal data to humans. This may result in uncertainties in toxicity values due to the differences in chemical absorption, metabolism, excretion, and toxic response between animals and humans. EPA takes into account differences in body weight, surface area, and pharmacokinetic relationships between animals and humans in order to minimize the potential for underestimating the dose-response relationship. However, conservatism is usually incorporated into each of these steps, which results in overestimation of potential risk.

- 2. *Extrapolation from one route of exposure to another route of exposure*—The SFs and RfDs often contain extrapolations from one route of exposure to another that result in additional conservatisms used in the risk calculations. For example, an extrapolation from the oral route to the inhalation and/or the dermal route was used to calculate SALs and baseline risks (EPA 2002, 76867), and differences between the two exposure pathways contribute to uncertainty in the estimation of potential risk at this site.
- 3. *Individual variability within the human population*—For noncarcinogenic effects, the degree of variability in human physical characteristics is important to determining the risks that can be expected at low exposures and to defining the no-observed-adverse-effect level (NOAEL). The NOAEL uncertainty factor approach incorporates a ten-fold factor to reflect individual variability within the human population which can contribute to uncertainty in a risk assessment; this factor of 10 generally results in a conservative estimate of risk for noncarcinogenic COPCs.
- 4. *Use of a surrogate to estimate COPC toxicity*—Several COPCs evaluated in the baseline risk assessment have no toxicity values in any of the databases. The reason for the lack of toxicity information is either that the chemical is not, or has not been, a concern, and/or the available toxicity information has not been reviewed by EPA. In these cases, there are several options available from, and recommended by, EPA: (1) addressing the potential risk in a qualitative manner, looking at magnitude of concentrations and frequency of detection; (2) calculating a value from available scientific literature using the EPA methodology; or (3) using a toxicity value for another chemical based on similar structure (EPA 1989, 08021). The assumption for the last alternative is that the known toxicity of one chemical may be used to estimate the toxicity of another structurally related chemical for which data are lacking. This alternative is often used because it allows the use of toxicity information that has been accepted by EPA and is more expeditious then trying to calculate a new toxicity value. The following surrogates were used for evaluating toxicity in this risk assessment: 2,6-DNT for 4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene, and RDX for DNX and MNX.

#### **6.2 Ecological Risk Assessment Summary**

Potential ecological risks were evaluated using multiple lines of evidence for the terrestrial and aquatic systems in Cañon de Valle. The detailed methodology and results for the ecological risk assessment are provided in Appendix L. The lines of evidence for the terrestrial system compare the small mammal populations and contaminant body burdens of Cañon de Valle with upper Pajarito Canyon (a reference site). The lines of evidence for the aquatic system make three comparisons. The first is a comparison of benthic macro-invertebrate communities between Cañon de Valle and three reference canyons. The second is a comparison of Cañon de Valle benthic macro-invertebrate data from 1997 with data from 2001. The third is a comparison of sediment toxicity in *Chironomus tentans* samples collected from Cañon de Valle with samples from a reference location in Starmer's Gulch.

## **6.2.1 Ecological Risk Assessment Methodology**

The process used to evaluate site conditions and to assess potential adverse ecological effects followed the guidance provided in EPA (1997, 59370) and NMED (2000, 70107). This process, as developed by the EPA, consists of eight generalized steps. The scoping and screening methodology developed by RRES-RS (LANL 1999, 64783) combines the first two steps of the EPA process. This results in seven ecological risk assessment steps:

- 1. RRES-RS ecological risk screening methodology (EPA Steps 1 and 2)
- 2. Baseline risk assessment problem formulation (EPA Step 3)
- 3. Sampling/study design and data quality objectives to address data gaps (EPA Step 4)
- 4. Field verification of the sampling design (EPA Step 5)
- 5. Site investigation (EPA Step 6)
- 6. Baseline risk characterization (EPA Step 7 )
- 7. Risk management (EPA Step 8)

The baseline ecological risk assessment approach for Cañon de Valle was developed in partnership with the NMED and DOE through the High Performing Team. The team meetings and field visits were used to receive feedback about the design, implementation, and results for Steps 1 through 6.

#### **6.2.1.1 Scoping, Screening and Problem Formulation**

The first and second steps of the process use ESLs that have been developed and documented in the Ecorisk Database. The screening analysis and problem formulation for Cañon de Valle were conducted using an earlier version, 1.2 (LANL 2000, 67822) of the database. These steps have not been revisited with the newer versions of the database because the conclusion of the problem formulation was a finding of potential adverse effects in the canyon. The consequence of identifying potential adverse effects in the canyon was to complete the ecological risk assessment process. Repeating the problem formulation with a newer version of the Ecorisk Database would not change that outcome. Step 1, ecological risk screening, is documented in LANL (1998, 59891). Step 2, baseline risk assessment problem formulation, is documented in Appendix L to this document.

# **6.2.1.2 Assessment Endpoints**

The problem formulation identifies the environmental values, or assessment endpoints, to be protected for Cañon de Valle, in the context of the surrounding landscape and the resident threatened species. Cañon de Valle is one of many canyons incised into the Pajarito Plateau. This canyon has a perennial spring and an alluvial seep in the vicinity of the TA-16 facilities. The presence of water in the canyon is ecologically important to the viability of many species in this semi-arid environment. Additionally, the canyon supports a multi-leveled overstory of mixed conifer, aspen, and oak, with grasses and forbs on overbanks and terraces. The combination of perennial water and diverse vegetation makes the canyon a relatively attractive location for endemic fauna. The Mexican spotted owl, a threatened species, has a nesting site downcanyon from the 260 outfall and is likely to hunt in the canyon. The following specific assessment endpoints are addressed by measures of effects identified in Step 3:

- Community viability of small mammals as an indication of contaminant impacts on maximally exposed taxa across trophic levels and foraging guilds in the terrestrial environment.
- Contaminant concentrations in the food web as an indication of potential impacts on carnivores, including the Mexican Spotted Owl, a resident threatened species in the canyon.
- Capacity of the perennial reach of the canyon to support an aquatic community as an indication of the extent to which contaminants have impaired sediment and water quality.

# **6.2.1.3 Study Design and Implementation**

The third step, sampling/study design and data quality objectives, develops those measures of effects to be used in field investigations that will provide lines of evidence to address the assessment endpoints. The design is coupled with Step 4, field verification, to determine the feasibility of the proposed sampling plan, and with Step 5, field investigation, to implement the study design. Terrestrial system lines of evidence consisted of small mammal population studies and small mammal contaminant body burdens. The aquatic system's lines of evidence consisted of benthic macro-invertebrate surveys and toxicity testing of site sediment and water. The details of Steps 3 through 5 can be found in Appendix L.

#### **6.2.1.4 Risk Characterization**

Step 6, baseline risk characterization, assembles the lines of evidence to determine whether adverse effects are occurring at the site, determines the extent of those effects, and makes a recommendation for risk management. The final step, risk management, is a policy and institutional management process that uses the results of the assessment and incorporates public comment. Step 6 is documented in Appendix L of this report. Risk management will be developed and documented in the CMI for the site.

#### **6.2.2 Ecological Risk Assessment Results**

#### **6.2.2.1 Terrestrial Assessment**

Results of the terrestrial mammal population study show that the number of species and the population densities are both greater in Cañon de Valle than in the reference site. Additionally, Cañon de Valle consistently had more reproductive status classes than Pajarito Canyon. This evidence indicates that the contaminant inventories in Cañon de Valle are not adversely affecting the small mammal community.

A comparison of body weights by species shows no differences between the canyons except in the case of brush mice when the sexes are combined (Appendix L, Table L-7). As detailed in Appendix L, this

difference in weights is associated with a relatively large number of nonreproductive individuals in Cañon de Valle. The difference in weights actually indicates the brush mouse population in Cañon de Valle is more active with regard to reproduction because it has more individuals making the transition from juvenile to reproductive status.

The analysis of contaminant body burdens for small mammals shows that the whole-mouse concentrations are well below concentration levels of concern [defined as ecological screening levels (ESLs)] for the Mexican spotted owl. The maximum lead value exceeded the ESL, but upper bound estimates for the median lead value and considerations of the owl home range indicate that the contaminant inventories in Cañon de Valle are not posing a potential food chain risk to the owl.

## **6.2.2.2 Aquatic Assessment**

The benthic macro-invertebrate lines of evidence for 1996 and 1997 show that the total number of benthic macro-invertebrate taxa in Cañon de Valle (31) is within the range of values for the three reference reaches (25 to 42). Sensitive species are present in Cañon de Valle, but the total number of sensitive species is lower than in the reference reaches. This result corresponds to the comparisons of community metrics for the reaches. The Cañon de Valle composite metric score of 81% is slightly above the cut-off for impacted streams (79%) when compared to Pajarito Canyon, the most similar reference stream. There are two possible sources of these differences. First, the scraper community is substantially reduced in Cañon de Valle. The primary reason is thought to be a lack of habitat to support that feeding strategy. When the community metrics are summed without the scraper community metric, Cañon de Valle scores 90% relative to Pajarito Canyon. The second source of differences between Cañon de Valle and the references reaches is stream size. Cañon de Valle is the smallest of the streams. It is common for smaller streams to have fewer taxa.

The 2001 benthic macro-invertebrate data from Cañon de Valle show general decreases from 1997 in numbers of species, sensitive species, and community metrics. These changes are primarily due to a combination of the elimination of flow augmentation by effluent discharges and the continuing drought which has reduced natural sources of water to the canyon. A toxicity test of the sediment and site water adjacent to the Cañon de Valle benthic macro-invertebrate sampling site indicated no adverse effects for the survival or growth of the test organism, *Chironomus tentans*. If the reduction in benthic macroinvertebrate community metrics were related to contaminants, one would expect survival and growth impacts in the toxicity test.

The sediment toxicity testing lines of evidence show that Cañon de Valle may be affected relative to the reference site in Starmer's Gulch. The greatest impacts occurred at the SWSC Cut site, with 22.5% survival and an increase in growth. The mortality is likely associated with silver in the sediment and water and with lead in the water column. The increase in growth over reference organisms is most likely associated with the presence of RDX in the sediment (Appendix L, Figures L-9 and L-10).

The toxicity testing site below the confluence with Burning Ground Spring showed a moderate survival response of 68.5% which was not different from the reference site but was statistically different (in this case, less than) from the downstream site below MDA P. The sediment at this location had elevated levels of barium, copper, and lead. The site below MDA P had survival and growth responses similar to the reference site at Starmer's Gulch.

In 2002, a second round of toxicity testing was conducted for the sites that had shown reduced survival in 2001. The mortality responses of 2001 did not recur (Appendix L, Table L-11). These results indicate that the sediment in the canyon is heterogeneous with regard to potential toxic effects and contaminant concentrations. The variability in the toxicity testing results is important to the risk characterization

because it helps to reconcile the lack of effects noted in benthic macro-invertebrate community data. If there are pockets of sediment that cause adverse effects in the aquatic community, these areas are likely to be small and avoidable by the benthic community.

## **6.2.2.3 Uncertainty Analysis**

The major source of uncertainty associated with this assessment is that the terrestrial and sediment toxicity evaluations were conducted during a multi-year drought and within 1 year of the Cerro Grande fire of 2000. The results of the investigations may differ during wetter periods, but the potential impact of contaminants on the environment is not likely to be increased. Individual and population effects are typically the consequence of multiple stressors. The drought is one of those stressors and is likely to increase the potential of detecting an adverse effect that could be associated with contaminants. Fire effects often result in increased small mammal populations associated with increased ground vegetation. If contaminant uptake and food chain transfers were a source of population effects, then post-fire environments should increase the likelihood of these effects.

Ecological screening assessments are subject to uncertainties through the use of laboratory toxicology studies to develop NOAEL contaminant concentrations. These studies use chemical forms of contaminants and exposure mechanisms that are often conservative when compared to environmental conditions and foraging behaviors. Additionally, laboratory studies are often conducted with single contaminants. The consequences of combined contaminants for receptors is largely unknown. The results presented for Cañon de Valle are based upon field studies and laboratory toxicity studies combined with field-collected media from the canyon. This approach obviates the usual difficulties of extrapolating laboratory data to field settings.

The calculations of HMX and RDX exposure concentrations for the Mexican spotted owl were based on mammal toxicity reference values. This is because, at the time this work was conducted, data were not available in the literature for avian exposures to these chemicals. The Department of the Army has since published results of exposure studies for RDX (Salice and Holdsworth 2001, 73780) and HMX (USACHPPM 2001, 73781) using Northern Bobwhite quail (*Colinus virginianus*)*.* The toxicity reference value (TRV) for RDX is 8.7 mg/kg-d. This value is in agreement with the rat TRV of 10 mg/kg-d, indicating that the calculated Mexican spotted owl ESL for RDX is appropriate. The companion study for HMX did not publish a TRV because exposure of quail to HMX has not resulted in mortality or morbidity in subchronic studies with doses up to 10,000 ppm HMX in food. These results indicate that the mouse TRV of 75 mg/kg-d for HMX is a conservative proxy for avian effects and is protective of the Mexican spotted owl.

The relevance of this assessment for making decisions regarding Cañon de Valle is predicated upon the assumptions that the data accurately represent the contaminant signatures in the canyon and that the present-day contaminant concentrations will be diminished in the future through hydrologic processes. The data have been collected over three phases of RFI, each phase responding to the results of previous work. The elimination of facility discharges, the removal and closure of MDA P, the excavation of the silver outfall, the IM conducted at the 260 outfall, and the partial removal of MDA R all lend support to the assumption that contaminant sources have been reduced or eliminated, and that contaminant concentrations in the canyon are likely to decrease over time.

The silver concentrations for sediment in the canyon, from the SWSC Cut and above, run contrary to this conceptual model. In 2001 and 2002, six ecotoxicological samples were collected in support of toxicity testing, and the 2002 active channel sediment samples contained silver concentrations ranging from 85.5 to 167 mg/kg. The previous high value for silver in Cañon de Valle across 45 samples with 25 detections

was 15.1 mg/kg. These high values in the channel, within 2000 ft of the silver outfall, indicate that post–Cerro Grande fire flooding or the removal action at the silver outfall mobilized silver downcanyon.

## **6.2.2.4 Summary of Ecological Risk**

The ecological risk assessment for the terrestrial system in Cañon de Valle revealed some elevated metals concentrations in the small mammals but no values that were likely to cause adverse effects for the Mexican spotted owl. The numbers of species, population densities, and reproductive classes for those species indicated that the Cañon de Valle small mammal community is not being adversely affected by contaminants.

The ecological assessment of the aquatic system in the canyon found some differences between benthic macro-invertebrates in Cañon de Valle and reference canyons. These differences were attributed to relative sizes of the streams, with Cañon de Valle being the smallest, and reduced flows due to the ongoing drought. One of the two rounds of toxicity testing for sediment and water in the canyon resulted in reduced survival for a site near the 260 outfall and a site below Burning Ground Spring. These results were not replicated in a subsequent toxicity test, indicating a high variability in the contaminant signatures for this sediment. Because the toxicity test is designed to be an indicator of potential effects in an aquatic system but is not a substitute for field assessments, the presence of a viable benthic macro-invertebrate community in the canyon may be a more meaningful measure of the canyon's condition than the toxicity testing results.

# **7.0 CONCLUSIONS**

In general, the overall conceptual model presented in the Phase II RFI still applies on a site-wide basis. The Phase III RFI data have reduced data uncertainties for the CMS process. One important goal of the Phase III RFI was to investigate and incorporate into the conceptual model the hydrogeologic and contaminant transport dynamics of the Cañon de Valle and Martin Spring alluvial and subsurface groundwater systems. The Phase III RFI conclusions are provided in the following sections.

#### **7.1 SWMU 16-021(c)-99 Source Area**

- The removal of over 1300 yd<sup>3</sup> of soil during the IM greatly reduced the source area concentrations of barium and HE compounds. Although the volume of the residual soil within the former outfall source area is less than 100 yd<sup>3</sup> (based on field observations), the soil contains elevated concentrations of HE and barium that could be mobilized by stormwater runoff. Although the residual soil is small in volume, approximately 650 kg of HE compounds and barium COPCs still remain at SWMU 16-021(c)-99 in isolated locations throughout the drainage channel.
- The baseline risk assessment for the source area used the list of identified COPCs and assessed potential exposures to an on-site environmental worker, a trail user, and a construction worker. The cumulative excess cancer risk to all human receptors from potential exposures to all COPCs in soil and tuff is slightly above, or less than, the  $1\times10^{-5}$  risk specified by NMED under both CTE and RME assumptions (the potential risk is within the EPA target risk range of 10<sup>-6</sup> to 10<sup>-4</sup>). Noncancer hazards are below an HI of 1.0 for CTE exposure assumptions and below, or slightly above, an HI of 1.0 for RME assumptions (the maximum HI is 2.0).

#### **7.2 Cañon de Valle and Martin Spring Canyon Alluvial Systems**

- Sediments in Cañon de Valle and Martin Spring Canyon represent a secondary source for HE and barium that is potentially mobilized by surface water and alluvial groundwater. Moreover, the perennial reach of Cañon de Valle alluvial groundwater provides a high potential for subsequent infiltration of mobilized contaminants.
- For the Cañon de Valle alluvial area, a trail-user exposure scenario was assessed. The cumulative excess cancer risk to the trail user from potential exposure to all COPCs in sediment and surface water is below the  $1\times10^{-5}$  target risk specified by NMED for both CTE and RME assumptions. Noncancer hazards are below a HI of 1.0 for both exposure assumptions.
- The ecological risk assessment followed EPA and NMED guidance. For the terrestrial system in Cañon de Valle, elevated metals concentrations were found in small mammals but not at levels that are likely to cause adverse effects for the Mexican spotted owl. The numbers of species, population densities, and reproductive classes for those species indicated that the Cañon de Valle small mammal community is not being adversely affected by contaminants. In Cañon de Valle, a viable benthic macro-invertebrate community is present, which is a meaningful indicator that site contaminants pose negligible ecological effects.
- For Martin Spring Canyon, COPC concentrations were less than, or within the range of, those found at the Cañon de Valle alluvial area, which has been determined to not pose a potential unacceptable risk to human receptors under the trail-user scenario. Therefore, conditions at Martin Spring Canyon do not pose an unacceptable human health risk.

• Although RCRA contaminant levels are within acceptable human health risk and ecological risk ranges in the alluvial systems, isolated areas of contamination exceed acceptable ranges and will be addressed in the CMS.

## **7.3 Mesa Vadose Zone**

- The isotopic differences in composition between mesa vadose zone groundwater and Cañon de Valle alluvial groundwater indicate that mesa groundwater probably comes from local precipitation and snowmelt on the mesa top, whereas Cañon de Valle alluvial groundwater is at least partially derived from spring flow which is recharged at higher elevations.
- Borehole sampling in the mesa vadose zone indicate no contamination in the unsaturated depth intervals in any boreholes except in the immediate vicinity of the TA-16-260 former settling pond. These results indicate that mesa vadose zone contamination is concentrated beneath source area SWMUs such as the former and current ponds and drainages (90s Line Pond, V-Site Pond, 30s Line Pond) on the mesa top. However, ephemeral groundwater in mesa vadose zone wells that are not located in the vicinity of the TA-16-260 former settling pond have shown contamination, indicating lateral movement (possibly through surge beds) of water and contaminants in the mesa subsurface. In addition, based on the oxygen and deuterium stable isotope results, mesa vadose zone groundwater from Well 16-02665 (Martin Spring Canyon) and Well 16-02669 (90s Line Pond), and surface water from the 90s Line Pond, all show evaporative signatures, but spring water does not. These results reinforce the presence of a mesa vadose zone groundwater flow regime dominated by fractures and surge beds and, in general, the importance of hydrologic heterogeneity at TA-16.
- Contaminant transport in the mesa vadose zone is dominated by a fracture or surge bed flow regime, of which contaminated springs are a known manifestation. After the IM source removal, a substantial source for this contamination is gone, although reductions in spring contaminant concentrations are not yet evident. To assess the importance of these pathways, more wells are planned in both the mesa vadose zone groundwater and the regional aquifer during CMS activities.

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*The following list includes all documents cited in the main body of this report. Some appendixes to this report contains their own reference lists. The parenthetical information following each reference provides the author, publication date, and ER ID number. This information is also included in text citations. ER ID numbers are assigned by the RRES-RS Records Processing Facility (RPF) and are used to locate the document at the RPF and, where applicable, in the RRES-RS project reference library titled "Reference Set for Operable Unit 1082."*

*Copies of the reference library are maintained at the NMED Hazardous Waste Bureau; the DOE Los Alamos Site Office; the US Environmental Protection Agency, Region 6; and RRES-RS. This library is a living collection of documents that was developed to ensure that the administrative authority has all material needed to review the decisions and actions proposed in this document. However, documents previously submitted to the administrative authority are not included.* 

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