LA-UR-05-2295 June 2005 ER2005-0156

# **Groundwater Background Investigation Report**



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## **Groundwater Background Investigation Report**

**June 2005** 



#### **EXECUTIVE SUMMARY**

The March 1, 2005, Compliance Order on Consent signed by the New Mexico Environmental Department (NMED), the Department of Energy, and the Regents of the University of California, and the State of New Mexico Attorney General requires the Los Alamos National Laboratory (the Laboratory) to prepare and submit a groundwater background investigation report. The Consent Order was issued pursuant to the New Mexico Hazardous Waste Act, New Mexico Statutes Annotated (NMSA) 1978, § 74-4-10, and the New Mexico Solid Waste Act, NMSA 1978, § 74-9-36(D). This report describes work completed in accordance with the Consent Order.

This report presents background concentrations for naturally occurring metals and general chemistry parameters in groundwater and provides the bases for these concentrations. This report provides a comprehensive, validated database of 566 inorganic, selected organic, stable isotope, and radionuclide analyses of 196 groundwater samples collected from 13 background springs and wells and two other sites located in and around the Laboratory. Background values were determined for the three groundwater types, including alluvium, perched-intermediate volcanics, and the regional aquifer occurring beneath the Pajarito Plateau and the Laboratory. The majority of groundwater samples were collected before the Cerro Grande fire of May 2000, but additional samples at several locations were collected after the fire.

The region considered in this investigation extends from the western edge of the Jemez Mountains eastward to the Rio Grande and from Frijoles Canyon northward to Garcia Canyon. The alluvial groundwater is represented by well LAO-B and Pine Spring. The perched-intermediate groundwater is represented by Seven Springs (Bandelier Tuff), Apache Spring (Tschicoma Formation), Water Canyon Gallery (Bandelier Tuff), upper Cañon de Valle (Bandelier Tuff), and well LAOI(A)-1.1 (Bandelier Tuff). The regional aquifer is represented by well Otowi-4 (Santa Fe Group), well Guaje-5 (Santa Fe Group), Spring 9B (Cerros del Rio basalt), Doe Spring (hydromagmatic deposits), Pajarito Spring (Spring 4A) (Totavi gravels), Spring 1 (Santa Fe Group), La Mesita Spring (Santa Fe Group), and Sacred Spring (Santa Fe Group). La Mesita Spring, representing the Rio Grande Valley as a separate hydrogeochemical system, and Pajarito Spring, containing low concentrations of perchlorate (0.5  $\mu$ g/L) and nitrate (as nitrogen) (1 mg/L) were not included as part of the remaining 13 sampling stations for statistical analyses. Statistical evaluation of these two springs has been conducted as two separate sites.

The term "background" is used in this report to refer to natural groundwater occurring at springs or penetrated by wells that have not been contaminated by the Laboratory or other municipal or industrial sources and that are representative of groundwater discharging from their respective host rocks or aquifer material. The sites are relatively easy to access and are readily sampled for chemical and radiochemical analyses. As a group, groundwater sampled as part of this investigation has low dissolved concentrations of major ions and trace elements (for example, chloride, nitrate, sulfate, boron, natural uranium). Atmospheric (fallout) tritium concentrations were detected in several springs discharging in the Sierra de los Valles, west and up (hydraulic) gradient of the Laboratory.

Spring sites are located around the periphery of the Laboratory. One spring site (Seven Springs) was chosen because it occurs roughly 30 km west of the Laboratory and discharges from the Bandelier Tuff (the most common rock type within Laboratory boundaries). Seven Springs water contains low concentrations of chemical solutes and anthropogenic tritium at levels approximately equal to that of precipitation in this region.

In 1997, 1998, 1999, and 2000, during six sampling events, filtered and nonfiltered water samples were collected and analyzed for chemical constituents and parameters. The samples had low turbidity values of less than five nephelometric turbidity units. Inorganic analytes include major ions, minor elements, and trace elements; organic solutes consist of naturally occurring humic substances (hydrophobic compounds) and small molecular-weight (hydrophilic) organic compounds; and natural and fallout-derived radionuclides. For each sample station, results of statistical analyses are provided for 9 major ion species; 39 trace element compounds; up to 3 stable isotopes of hydrogen, nitrogen, and oxygen; tritium; hydrophobic and hydrophilic organic compounds associated with dissolved organic carbon fractionation; 11 radiological isotopes; and gross alpha, beta, and gamma radionuclides.

The hydrochemistries of background alluvial and perched groundwater and the regional aquifer differ from each other. Variations in natural groundwater compositions within the three aquifer types are controlled by adsorption/desorption and precipitation/dissolution reactions, aquifer composition of reactive minerals and amorphous solids, solute residence times, types of microbial populations, and lengths of groundwater flow paths. Groundwater compositions include calcium-bicarbonate type water for alluvial and perchedintermediate aquifers. The regional aquifer ranges from a calcium-sodium-bicarbonate to a sodiumcalcium bicarbonate type water. Alluvial and perched-intermediate groundwaters occur within the vadose zone above the regional water table.

Native alluvial groundwater contains the lowest total dissolved solids (TDS) with calcium, sodium, silica, and bicarbonate as the dominant solutes. Concentrations of major ions and trace elements also vary seasonally in response to recharge water consisting of snow melt, storm events, and base flow. Background activities of tritium exceed 30 pCi/L within alluvial groundwater.

Perched intermediate groundwater is characterized by higher TDS in comparison to alluvial groundwater. Concentrations of magnesium generally are the highest within perched zones. Background intermediate stations within the Sierra de los Valles sampled during this investigation contain tritium derived from the atmosphere (cosmogenic and residual bomb pulse). Perched intermediate groundwater beneath the Pajarito Plateau, however, contains background activities of tritium less than 2 pCi/L.

The natural aqueous geochemistry of the regional aquifer is characterized by residence times exceeding 10,000 years. The regional aquifer contains the highest natural concentrations of TDS, calcium, sodium, bicarbonate, barium, boron, and uranium in comparison to alluvial and perched-intermediate groundwater. Native groundwater within the regional aquifer most commonly contains less than 1 pCi/L of tritium.

The statistical analyses of the background data involve the use of several exploratory data analysis (EDA) tools. These tools include normal quantile plots of untransformed data, box plots to compare possible data groups, linear regression analysis and scatter plots, and statistical data summaries. The purpose of EDA is to identify possible outliers in these data, understand relationships between analytes, evaluate parametric and nonparametric statistical modeling options, and determine the frequency of nondetect values by analyte and by potential data subpopulations. Differences in water chemistry as a result of sample preparation, analytical methods, and aquifer type are evaluated for each analyte. Spatial and temporal trends in these data are also assessed.

The data provided here include field duplicate samples collected in the investigation and three samples collected by the NMED at the selected stations. An additional 56 water samples collected by NMED and analyzed for low-level perchlorate using liquid chromatography/ mass spectrometry/mass spectrometry have been statistically evaluated and results included as part of this investigation. These samples were collected from springs discharging within the Sierra de los Valles and White Rock Canyon. A single sample for the Rio Grande is also included in this statistical summary for geochemical comparison.

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## **1.0 INTRODUCTION**

## **1.1 Rationale for Investigation**

The March 1, 2005, Compliance Order on Consent signed by the New Mexico Environmental Department (NMED), the Department of Energy (DOE), and the Regents of the University of California, and the State of New Mexico Attorney General requires the Los Alamos National Laboratory (the Laboratory) to prepare and submit a groundwater background investigation report. The Consent Order was issued pursuant to the New Mexico Hazardous Waste Act, New Mexico Statutes Annotated (NMSA) 1978, § 74-4-10, and the New Mexico Solid Waste Act, NMSA 1978, § 74-9-36(D). This report describes work completed in accordance with the Consent Order.

This report presents background concentrations for naturally occurring metals and general chemistry parameters in groundwater and provides the basis for these concentrations. Background hydrogeochemical data requirements are also addressed in the "Hydrogeologic Workplan," Sections 1.0 and 4.0 (LANL 1998, 59599), and within individual work plans prepared by the Environmental Stewardship–Environmental Remediation and Surveillance (ENV-ERS) Program. This background investigation is further addressed in the Groundwater Protection Management Program Plan, Section 4.0, Groundwater Protection Efforts at the Laboratory, and Section 5.0, Issues and Solutions (LANL 1996, 70215).

Background hydrogeochemical data with corresponding statistical information are required to distinguish between contaminated and noncontaminated waters for environmental investigations conducted at the Laboratory. Background hydrogeochemical data also provide information for environmental risk assessments; for Resource Conservation and Recovery Act (RCRA) site investigations; for evaluating hydrogeochemical processes occurring along groundwater flow paths; for defining recharge zones and hydrological pathways; and for establishing cleanup levels during the remediation of contaminated waters at the Laboratory.

## **1.2 Scope of Report**

This report provides background hydrogeochemical data for the alluvial, perched-intermediate, and regional groundwater systems beneath the Pajarito Plateau and the Laboratory. It includes a comprehensive validated database of 566 natural inorganic and organic chemical, stable isotope, and radionuclide analyses of 196 groundwater samples collected from 13 background springs and wells and two other sites located in and around the Laboratory. The term "background" as used here refers to natural waters discharged by springs or penetrated by wells that have not been contaminated by Laboratory effluent or other municipal or industrial activities and that are representative of groundwater discharging from its respective aquifer material.

The region considered in this investigation extends from the western edge of the Jemez Mountains eastward to the Rio Grande and from Frijoles Canyon northward to Garcia Canyon. Figure 1.2-1 shows the fifteen stations sampled for this investigation. The choice of sampling sites was made by the authors using previously published knowledge of the Jemez Mountains/Pajarito Plateau region (Vuataz and Goff 1986, 73687; Shevenell et al. 1987, 06673; Shevenell and Goff 1995, 73689; Adams et al. 1995, 47192; and Blake et al. 1995, 49931). The locations of sampling sites were discussed with the NMED (Dale 2005, 88774). Based on these discussions, eleven springs and four wells were chosen, and the sites were separated into three aquifer material types: alluvium, perched-intermediate-depth volcanic rocks, and the regional aquifer sediments.

The sampling stations and associated aquifer types are listed below.

#### *Alluvium*

Well LAO-B and Pine Spring were selected as being representative of groundwaters in alluvial aquifers. Although a portion of groundwater that discharges at Pine Spring flows through the Puye Formation and lavas of the Polvadera Group, water samples were collected from the alluvium at the point of discharge.

#### *Perched Intermediate Volcanic Rocks*

Four springs or groups of springs and one well were selected as being representative of groundwaters in the perched-intermediate system. They are the Water Canyon Gallery (Bandelier Tuff), Seven Springs (Bandelier Tuff), Apache Spring (Tschicoma Formation), upper Cañon de Valle Spring (Bandelier Tuff), and well LAOI(A)-1.1 (Bandelier Tuff).

#### *Regional Aquifer*

Six springs and two wells were selected as being representative of groundwaters in the regional aquifer. They are La Mesita Spring (Santa Fe Group sediments), Spring 1 (landslide blocks in Cerros del Rio basalt, Santa Fe Group sediments, and Totavi Lentil), Sacred Spring (Santa Fe Group sediments), Doe Spring (phreatic [hydro]-magmatic deposits), Spring 9B (Cerros del Rio basalt), Pajarito Spring (4A) (landslide blocks in Cerros del Rio basalt and Totavi Lentil), supply well Otowi-4 (Santa Fe Group), and supply well Guaje-5 (Santa Fe Group).

#### **1.3 Objectives**

The primary objective of this report is to provide background hydrogeochemical background concentrations for naturally occurring analytes for the three groundwater systems beneath the Pajarito Plateau and the Laboratory. Secondary objectives of this investigation include the following:

- 1. to review available background hydrogeochemical data collected at the Laboratory and surrounding areas before 1997 to provide a technical basis for investigations conducted from 1997 to 2000;
- 2. to compile additional groundwater data from background stations (springs and wells) sampled in 1997 to 2000 and afterward for alluvial and perched-intermediate groundwater and the regional aquifer;
- 3. to provide confidence in results of the analyses by comparing interlaboratory values; and
- 4. to provide statistical distributions for the different analytes occurring within alluvial and perchedintermediate groundwater and the regional aquifer.

#### **1.4 Methods**

For the main body of data from 1997 to 2000, filtered and nonfiltered water samples were collected and analyzed for chemical constituents and parameters during six sampling events in 1997, 1998, 1999, and 2000. Inorganic chemicals analyzed included major ions, minor elements, and trace elements; organic solutes consisting mainly of naturally occurring humic substances (hydrophobic compounds) and small molecular weight (hydrophilic) organic compounds; and natural and fallout-derived radionuclides. The analytes fall into one or more of the following three categories: (1) RCRA metal or target analyte; (2) hydrogeologic framework indicators relevant to a geochemical conceptual model; and (3) analytes present in Laboratory discharge and not RCRA metals. These three categories are based on regulatory and scientific perspectives that serve to make decisions regarding the nature and extent of contamination and provide an understanding of geochemical reactions occurring along flowpaths within alluvial and perched-intermediate groundwater and within the regional aquifer. Trace elements such as arsenic, barium, chromium, and uranium fall into category 1, but these analytes plus calcium, total organic carbon, stable isotopes, and bromide are of interest to category 2. Category 3 includes bicarbonate, sodium, calcium, and other constituents that are of site interest and are lacking MCLs.

For each sample station, results of statistical analyses are provided in this report for 9 major ion species; 39 trace elements; up to 3 stable isotopes of hydrogen, nitrogen, and oxygen; tritium; hydrophobic and hydrophilic organic compounds associated with dissolved organic carbon (DOC) fractionation; and 11 radiogenic isotopes, including gross alpha, beta, and gamma radiological measurements. Anthropogenic organic compounds such as trichloroethene (TCE), high-explosive (HE) compounds, polychlorinated biphenyls (PCBs), and other volatile and semivolatile chemicals were not included as part of this investigation because they were deemed to be introduced and are not indicative of background or natural values. Because technetium-99 is synthetically prepared, it also was not analyzed as part of this investigation.

Various statistical and design methods were developed for the assessment of background groundwater data. Section 4 of this report provides details and results of statistical analyses of groundwater samples collected as part of this investigation in 1997 and afterward. The assessment factors in the requirement that certain U.S. Environmental Protection Agency (EPA) and NMED regulations specify the location, frequency of sampling, and laboratory analytical methods for groundwater contaminant monitoring. From the statistical analyses, supported by confidence in interlaboratory comparisons, values for different analytes in each groundwater system could be determined.

The Cerro Grande fire burned several major watersheds west of and within the Laboratory in May 2000. These include Guaje Canyon, Pueblo Canyon, Los Alamos Canyon, Sandia Canyon, Mortandad Canyon, Pajarito Canyon, and Cañon de Valle. Section 2.2.2.4 discusses the short-term impact of the fire on springs and wells in those canyons. Sampling of springs, surface water, and alluvial groundwater from 2001 to 2003 has shown that most analytes have decreased to concentration levels before the fire (Gallaher and Koch 2004, 88747).

## **2.0 BACKGROUND**

## **2.1 Regional Geologic Framework and Conceptual Hydrogeologic Framework**

An understanding of the regional geologic framework is key to developing a conceptual model for hydrology. The hydrogeologic setting of springs and wells and controls on the mode of groundwater occurrence (alluvial, perched-intermediate, and regional aquifer) place constraints on groundwater residence times (more rapid fracture versus slower porous media flow). These variables can influence major ion and trace element aqueous chemistry through adsorption/desorption and precipitation/dissolution reactions.

A technically defensible conceptual hydrogeologic model is essential for characterizing background hydrochemistry, for selecting suitable sampling sites, and for correctly ascribing the sites to various parts of the hydrologic system. To develop the conceptual hydrogeologic model presented in Section 2.1.5, it is necessary to understand the geologic framework of the region and how it controls the occurrence and movement of groundwater. This geologic framework is presented in Sections 2.1.1 through 2.1.4.

## **2.1.1 Previous Work, Regional Geology**

The Pajarito Plateau lies on the east flank of the Jemez Mountains and on the west margin of the Española Basin (Figure 2.1-1). For the hydrogeologic discussions that follow, the Pajarito Plateau and underlying rock units are considered as a geologic feature of the Española Basin segment of the Rio Grande Rift (Manley 1979, 11714). The upper surface of the Pajarito Plateau, however, is composed primarily of the eroded top of the Tshirege Member of the Bandelier Tuff, a large-volume rhyolitic ash-flow tuff (ignimbrite) erupted from the Valles Caldera of the Jemez volcanic field (Smith and Bailey 1966, 21584).

Regional geologic maps that cover all or part of the Pajarito Plateau include those of Griggs (1964, 08795) for hydrogeologic investigations centered around Los Alamos; Smith et al. (1970, 09752) for volcanologic investigations of the Jemez Mountains; Kelley (1978, 11659) for tectonic investigations associated with the Rio Grande Rift; and Rogers (1995, 54419) for Laboratory waste management studies. Several geologic maps of nearby areas focus on a variety of subjects in the Española Basin/Pajarito Plateau region. They include those of Galusha and Blick (1971, 21526); Aubele (1978, 86539); Dethier and Manley (1985, 21506); Goff et al. (1990, 21574; 2002, 88776); and Dethier (1997, 49843).

Detailed geologic studies of the Bandelier Tuff are found in Broxton and Eller (1995, 58207). Syntheses of geology and tectonics on the Pajarito Plateau have been published by Dransfield and Gardner (1985, 06612) and Gardner and House (1987, 06682) as part of Laboratory investigations of the seismic hazard potential. Gardner et al. (1993, 12582; 1998, 63496) described drilling results around the Laboratory and high-precision mapping along the Pajarito fault zone. Collections of papers discussing geologic, geochemical, geophysical, and environmental aspects of the Jemez Mountains, Pajarito Plateau, and Rio Grande Rift are found in Riecker (1979, 21502); Baldridge et al. (1984, 88745); Keller (1986, 88740); and Goff et al. (1996, 56025). Geology and cross sections of the Frijoles 7.5-minute quadrangle, on which most of the Laboratory is found, was published by Goff et al. (2002, 88776).

## **2.1.2 Regional Tectonic Setting**

The Pajarito Plateau lies on the west side of the Española Basin, one of several late Tertiary basins of the Rio Grande Rift (Chapin 1979, 00597). Figure 2.1-2 shows generalized geologic relations beneath the Pajarito Plateau. The Rio Grande Rift is a major tectonic feature stretching from Colorado to northern Mexico and first developed about 25 to 30 Ma (million years ago). The Rio Grande Rift is characterized by crustal extension with predominantly normal faults, elevated seismicity along faults within and along margins of the basins, large negative gravity anomalies indicating thick basin fill, high conductive heat flow (to 120 megawatts/meter<sup>2</sup> [MW/m<sup>2</sup>]), and localized basaltic volcanism. Within the Pajarito Plateau region, the rift is bounded on the west by the Colorado Plateau and on the east by the Sangre de Cristo range, part of the southern Rocky Mountains (Aldrich 1986, 21497) (Figure 2.1-1). Because of similarities in age and tectonic style, the rift is considered by some to be a part of the southern Basin and Range tectonic province (Kelley 1978, 11659).

The transverse structural zone separating the Española Basin from the southern end of the San Luis Basin (Figure 2.1-3) (Broxton and Vaniman 2005, 88707) is called the Embudo fault zone. This fault is but one structural element of a major northeast-trending crustal discontinuity called the Jemez Lineament. As originally defined, the Jemez Lineament consists of an alignment of Miocene to Quaternary volcanic centers stretching from western Arizona to southeastern Colorado (Mayo 1958, 21573). No systematic trends in eruption ages or magma compositions are apparent among the various volcanic centers. By far

the largest volcanic center is the Jemez volcanic field, which has formed at the intersection of the Jemez Lineament and the Rio Grande Rift.

The transverse structural zone separating the Española Basin from the northern Albuquerque-Belen Basin (sometimes called the Santo Domingo Basin) is the northwest-trending La Bajada fault zone (Figure 2.1-3). The largest zone of rift-related basaltic volcanism occurs in the Cerros del Rio volcanic field located primarily north of and along the La Bajada fault zone (Figure 2.1-3). The Cerros del Rio field, referred to in some reports as "Basalt of Chino Mesa," is considered by some to be a peripheral part of the greater Jemez volcanic field (Smith et al. 1970, 09752). Volcanic rocks from both the Cerros del Rio and Jemez volcanic centers interfinger with sedimentary rocks filling the Española Basin beneath the Pajarito Plateau.

## **2.1.3 Regional Volcanism**

The evolution of the Jemez and Cerros del Rio volcanic fields has been outlined by Gardner and Goff (1984, 44021); Gardner et al. (1986, 21527); Self et al. (1986, 21579); Goff et al. (1989, 54783); Dunker et al. (1991, 88739); and WoldeGabriel et al. (1996, 54427). Volcanic rocks of the Jemez Mountains can be subdivided into three major groups named from the oldest to the youngest: the Keres, Polvadera, and Tewa Groups (Figure 2.1-4) (Broxton and Vaniman 2005, 88707). Volcanic rocks of the Keres Group consist of mafic basalt through silicic rhyolite in composition, although the unit is dominated volumetrically by intermediate-composition andesite. Published ages for the Keres Group range from about 13 to 6 Ma (Gardner et al. (1986, 21527). Rocks of the Polvadera Group also consist of basalt through rhyolite, but the dominant rock type is dacite and the published ages range from about 14 to 2 Ma (Gardner et al. (1986, 21527). Rocks of the Tewa Group consist almost exclusively of rhyolite, and they range in age from 1.75 to 0.06 Ma (Gardner et al. 1986, 21527; Goff et al. 1989, 54783). In general, a progression can be seen from mostly mafic to exclusively rhyolitic compositions with time in the main (or central) Jemez volcanic field.

Rocks of the Cerros del Rio field are not formally included within the three major groups of Jemez volcanic rocks. Cerros del Rio rocks compositionally consist of basalt and subordinate evolved rocks (hawaiite, mugearite, benmoreite, and dacite) ranging in age from 4.6 to <1.2 Ma (Bachman and Mehnert 1978, 88741; Dunker et al. 1991, 88739; WoldeGabriel et al. 1996, 54427). The most comprehensive study to date has focused on White Rock Canyon where the ages range from 2.8 to 2.3 Ma (WoldeGabriel et al. 1996, 54427). These authors have also dated a single lava flow at the bottom of the canyon just south of the mouth of Ancho Canyon at 9.3 Ma, a date consistent with ages of the Santa Fe Group.

Volcanism began in the Pajarito Plateau region about 16.5 to 14 Ma as small-volume eruptions of basalt that can be observed interbedded with older sedimentary rocks of the Española Basin both southwest and north of the Plateau (Dethier and Manley 1985, 21506; Gardner et al. 1986, 21527; Goff et al. 1990, 21574; Aldrich and Dethier 1990, 49681). During the period from 10 to 7 Ma, the major volume of Jemez volcanic rocks was erupted, mostly as andesite domes and flows in the central and southern Jemez Mountains (estimated volume 1000 km<sup>3</sup>). Smaller volumes of predominately dacite (about 500 km<sup>3</sup>) were vented during the period 7 to 2.5 Ma (Gardner et al. 1986, 21527; Goff et al. 1989, 54783). The Sierra de los Valles west of Los Alamos consists of these dacitic domes and flows. During these voluminous andesitic and dacitic phases, large debris aprons of volcaniclastic rocks (Cochiti and Puye Formations) were shed eastward into the Española Basin. These deposits interfinger with axial sediments of the basin. Lavas within the entire compositional range of the Cerros del Rio were erupted primarily from 4 to 2 Ma and formed cinder cones, shield lavas, intercanyon flows, and maar deposits. The latter interfinger with dacitic rocks, fan deposits, and fluvial sediments in the basin fill beneath the Pajarito Plateau.

## **2.1.4 Pajarito Plateau Stratigraphy**

Figure 2.1-4 (Broxton and Vaniman 2005, 88707) shows the most recent representation of the stratigraphy of the Pajarito Plateau. Stratigraphic nomenclature on the Pajarito Plateau has been refined many times during the last 50 years (Denny 1940, 88738; Spiegel and Baldwin 1963, 54259; Griggs 1964, 08795; Baltz et al. 1963, 08402; Bailey et al. 1969, 08406; Galusha and Blick 1971, 21526; Manley 1979, 11714; Purtymun 1995, 45344). Griggs's nomenclature was based on mapping and lithologic descriptions of water well cuttings on Laboratory property. Griggs's nomenclature has continued to be used in later hydrogeologic investigations conducted by Laboratory personnel as additional water wells were drilled (Dransfield and Gardner 1985, 06612). These authors combined well data with geophysical investigations and surface mapping to produce a structure contour map of the top of the pre-Bandelier Tuff surface (ca 1.6 Ma). Dransfield and Gardner (1985, 06612) provide information that the pre-Bandelier topography beneath the Pajarito Plateau is dominated by dacitic rocks of the Polvadera Group in the west, fanglomerates of the Puye Formation in the northeast, and mafic shield volcanoes and flows of the Cerros del Rio volcanic field in the southeast.

The stratigraphy of three deep (>600 m) wells on the Pajarito Plateau was compiled by Goff (1995, 49682), based on lithologic descriptions of Stoker et al. (1992, 12017) and Purtymun et al. (1993, 15371). Detailed stratigraphy of several recent characterization wells has been documented in a series of Laboratory reports (i.e., Broxton et al. 2001, 71251; Broxton et al. 2001, 71252; Ball et al. 2002, 71471).

Generalized cross sections of Pajarito Plateau stratigraphy may be found in Turbeville et al. (1989, 21587), Purtymun (1995, 45344), and Robinson et al. (2005, 88767). Four detailed cross sections projected through different sectors of the Pajarito Plateau are shown in Goff et al. (2002, 49682). These sections use stratigraphic data from many of the observation wells. Goff et al. (2002, 49682) also provide detailed lithologic descriptions of the primary rock units in the region (Table 2.1-1).

## **2.1.5 Conceptual Hydrogeologic Model**

The current conceptual hydrogeologic model for the Pajarito Plateau is a synthesis of much previous hydrologic work spanning many years. The growth of the Laboratory, as well as Los Alamos townsite, led to various investigations that characterized general hydrology of the Pajarito Plateau and water chemistry of springs discharging within White Rock Canyon (Purtymun et al. 1980, 00208, Purtymun and Johansen 1974, 11835); the hydrogeology of the Bandelier Tuff and other rock units (Rogers and Gallaher 1995, 48845; Abeele et al. 1981, 06273) and water supply wells (Theis and Conover 1962, 11878; Griggs 1964, 8795; Cushman 1965, 08584; Purtymun 1975, 11787; Purtymun 1984, 06513; Purtymun and Cooper 1969, 11831). Concerns over the occurrence of, or potential for, groundwater contamination by wastedisposal practices at the Laboratory prompted additional hydrogeologic studies (Baltz et al. 1963, 08204; Purtymun et al. 1966, 09653; DeVaurs and Purtymun 1985, 07415; Stoker et al. 1991, 07530). Pathway analysis (Geologic, Inc. 1989, 31492) and numerical modeling studies have further contributed to understanding both shallow and deep, local and regional, unsaturated and saturated groundwater systems at Los Alamos (Hearne 1985, 88749; McAda and Wasiolek 1988, 88737; Umari and Szeliga 1989, 88735; Koenig and McLin 1992, 56029; Geddis 1992, 31592; Frenzel 1995, 56028; Stone 1995, 56043; Birdsell et al. 1995, 70012; Gray 1997, 58208; Dander 1998, 88743; Keating et al. 1999, 88746).

In spite of this previous work, the conceptual hydrogeologic model for the Pajarito Plateau and the Laboratory is continuously being refined (Stone 1996, 63989; Robinson et al. 2005, 88767). However, the 25 deep (regional aquifer) wells installed under the "Hydrogeologic Workplan" (LANL 1998, 59599) have contributed much-needed information (Robinson et al. 2005, 88767). The next subsections provide an

overview of the hydrogeologic model, including groundwater occurrence and movement, and serve as the framework for the hydrogeochemical model discussed in Section 2.2.

## **2.1.5.1 Overview**

The simplest conceptual hydrogeologic model for the Pajarito Plateau and the Laboratory includes saturated porous media in which the surface of saturated zone(s) mimics topography. For example, the regional water table slopes eastward from a recharge zone in the Sierra de los Valles west of the Laboratory toward the Rio Grande groundwater discharge zone. Complicating this simple model, however, are zones of saturation perched above the regional water table in shallow alluvium and perched-intermediate-depth volcanic rocks (Purtymun 1995, 45344).

## **2.1.5.2 Groundwater Occurrence**

Groundwater occurrence is generally described in terms of geography. For example, groundwater may be more accessible or plentiful in one area than in another, perhaps as a result of changes in aquifer thickness and sedimentary facies within the aquifer or the hydrogeologic unit. Although groundwater productivity in supply wells varies with the hydrogeologic unit making up the regional aquifer, the depth to the water table is primarily the result of topography. The regional zone of saturation is more accessible in canyons than on mesas.

The occurrence of groundwater is more commonly described in terms of stratigraphy (the saturated hydrogeologic unit), hydrologic condition (unconfined or confined), and scale (local perched or regional saturation). At the Laboratory, groundwater has been observed to occur in three modes:

- perched at shallow depth (alluvium in canyon bottoms),
- perched at intermediate depth (the Guaje Pumice Bed, Cerros del Rio basalt, Tschicoma Formation, and Puye Formation), and
- at greater depth within various units that make up the regional aquifer (Tschicoma Formation, Cerros del Rio basalt, Puye Formation, and Santa Fe Group), depending on the location.

Figure 2.1-5 depicts a conceptual hydrogeologic model for canyon settings, which includes alluvial and perched-intermediate groundwater and the regional aquifer. Groundwater in the perched zones is generally unconfined. Groundwater in the regional zone of saturation is also generally unconfined, but confined conditions have been documented in older supply wells in lower Los Alamos Canyon (Purtymun 1995, 45344). Some springs discharging in and near lower Los Alamos Canyon (Sacred Spring, Spring 1, and La Mesita Spring) are also probably artesian.

Perching of groundwater in the shallow and intermediate-depth zones occurs in different ways. The occurrence of perched water in the alluvium is restricted to canyon floors, and saturation does not appear to extend beneath the adjacent mesas. In alluvial environments, infiltration and percolation of stream flow readily recharge the zone of perched saturation. Ephemeral streams, such as those occurring in canyons at the Laboratory, lose much water along their courses (transmission loss). The weathered Bandelier Tuff underlying the alluvium is less permeable and provides a perching layer or aquitard.

The occurrence of intermediate-depth perched groundwater in the Cerros del Rio basalt and other hydrostratigraphic units is less readily explained. Perching at intermediate depths requires the downward percolation of groundwater through the alluvium and the Bandelier Tuff, which suggests that the Bandelier Tuff is capable of transmitting groundwater. In places where the Bandelier Tuff is absent, having been scoured out by stream flow, no low-permeability barrier exists between the alluvium and underlying units.

This is the case in Los Alamos Canyon east of the confluence with DP Canyon, where the Bandelier Tuff is missing and where alluvium rests directly on the permeable deposits of the Puye Formation (LANL 2004, 87390). Perching of intermediate-depth groundwater is caused by the presence of less permeable material, including massive basalt and basaltic tephra, as observed at well R-9 (Broxton et al. 2001, 71250); clay-rich lake beds encountered at R-12 (Broxton et al. 2001, 71252); or clay-rich rock observed at R-15 (Longmire et al. 2001, 70103).

The regional water table occurs within the Puye Formation and Santa Fe Group beneath the Pajarito Plateau. The slope of the regional water table decreases to the east (Figure 2.1-6) and is influenced by pumping wells. Groundwater in the regional aquifer discharges as springs in White Rock Canyon. The hydraulic gradient within the regional aquifer east of the Sierra de los Valles is downward, and overlying alluvial and perched-intermediate groundwater systems provide recharge to the regional aquifer (Broxton et al. 2002, 76006). Groundwater flow rates within the regional aquifer vary, depending on the grain size of the aquifer material, hydraulic conductivity, and hydraulic gradient. Flow within the regional aquifer occurs under porous (wells R-25, R-19, R-15, R-13, R-14) and fracture (R-26, R-9, R-12) conditions.

## **2.1.5.3 Groundwater Movement**

The movement of groundwater consists of three basic elements: recharge, flow, and discharge. Recharge and discharge each involve an area, a process, and a rate, but flow involves a direction and a rate.

## **2.1.5.3.1 Recharge**

Groundwater flows from areas of higher-pressure potentials (west) to areas of lower potentials (east) (Figure 2.1-6), indicating that recharge occurs in the higher elevations (Sierra de los Valles) west of the Laboratory, probably in response to the higher amounts of precipitation at these higher elevations. Recharge processes include the infiltration of rainfall, snowmelt, or runoff and then deep percolation of any moisture that escapes evapotranspiration. Recharge is especially effective along stream channels, where larger volumes of water occur at any given place and time. Recharge of the shallow, intermediate, and deep groundwater systems probably occurs at different rates.

## **2.1.5.3.2 Flow**

From limited hydrologic data and information, groundwater flow direction seems to be the same for the shallow, intermediate, and deep systems. In canyons where numerous wells have been drilled to allow for observations, such as in Mortandad Canyon, the water table for the shallow groundwater perched in the alluvium slopes toward the east, as does the canyon floor (Stone 1995, 56043). The intermediate-depth perched groundwater zones are still too poorly bounded to characterize flow direction with any certainty. As shown by Figure 2.1-6, groundwater flow in the regional aquifer generally is to the east and southeast toward the Rio Grande.

The rate of groundwater flow depends on the hydraulic properties of the various saturated materials beneath the Pajarito Plateau. The actual flow rate or groundwater velocity (v) at a given point of interest depends on the hydraulic conductivity  $(K)$  for the material, effective porosity  $(n_e)$ , and the slope of the water table or hydraulic gradient (I), according to Darcy's law (Freeze and Cherry 1979, 88742):

 $v = K1/n_e.$  (1)

Hydraulic conductivity values, however, are a proxy for at least the potential rate of groundwater flow. Sparse data for K are available from hydrologic testing of observation, water supply, test, and regional characterization wells in the area. The mean K value for the alluvium in Los Alamos Canyon, based on slug tests in nine observation wells, is  $9.6 \times 10^{-3}$  cm/s with an error of  $\pm 10\%$  (Gallaher 1995, 49679). Laboratory testing of cores from two wells in Mortandad Canyon yielded saturated K values of  $5 \times 10^{-5}$  to 1 x 10<sup>-3</sup> cm/s for the Tshirege Member (unit 1A) of the Bandelier Tuff and 7 x 10<sup>-5</sup> to 1 x 10<sup>-3</sup> cm/s for the Tsankawi Pumice Bed (Stoker et al. 1991, 07530). Aquifer performance data for deeper units are available from pumping tests conducted on water supply and test wells. Unfortunately, some of the wells are screened across more than one stratum, and K values for specific geologic units at these locations are not available. Hydraulic conductivity values obtained from pumping tests conducted on water supply and test wells screened in a single unit vary by one to two orders of magnitude: 4 to 241 gal./day/ft<sup>2</sup> for the Puye Formation and 3 to 11.3 gal./day/ft<sup>2</sup> for the Santa Fe Group (Purtymun 1995, 45344). More recent testing in characterization wells installed under the "Hydrogeologic Workplan" (LANL 1998, 59599) has provided K values of 2.79 x 10<sup>-3</sup> to 1.31 x 10<sup>-2</sup> cm/s for intervals of the Cerros del Rio basalt at well R-9i (Broxton et al. 2001, 71251); 7.27 x 10<sup>-4</sup> cm/s for the Puye Formation at well R-15 (Longmire et al. 2001, 70103); 6.17 x 10<sup>-3</sup> and 6.91 x 10<sup>-3</sup> cm/s for the Santa Fe Group at well R-19 (Broxton et al. 2001, 71254); 2.32 x 10<sup>-3</sup> and 1.28 x 10<sup>-3</sup> cm/s for the Cerros del Rio basalt at well R-31 (Vaniman et al. 2002, 72615); and 8.21 x 10<sup>-3</sup> cm/s for the Puye Formation at well R-31 (Vaniman et al. 2002, 72615).

Radiocarbon dating of groundwater is another method of calculating flow rates, although it is difficult to collect groundwater samples not impacted by atmospheric carbon dioxide. Such dating of regional aquifer groundwater at the Laboratory suggests preliminary flow rates ranging from a minimum of 1.93 x 10<sup>-5</sup> cm/s for the Tesuque Formation in lower Los Alamos Canyon to a maximum of 3.33 x 10 $4$  cm/s for the Puye Formation, in the area between Water Canyon and upper Ancho Canyon (Purtymun 1984, 06513).

## **2.1.5.3.3 Discharge**

Alluvial, intermediate, and regional aquifer groundwaters discharge in different ways, depending on hydrogeologic conditions. Alluvial groundwater is either forced to the surface by bedrock highs where it supports stream flow for some distance downcanyon or it seeps into the underlying hydrogeologic unit. Intermediate-depth perched groundwater either discharges eventually at downgradient springs along canyon walls or continues to percolate downward toward the regional water table. Regional groundwater discharges at springs within White Rock Canyon.

## **2.2 Conceptual Hydrogeochemical Model**

This section presents a conceptual hydrogeochemical model for the Pajarito Plateau, which focuses on natural distributions of inorganic and organic solutes or dissolved species. This model is based on geochemical data collected to date and includes water chemistry and mineralogy of aquifer material. This conceptualization is essential for characterizing background and site hydrochemistry and includes a hydrogeologic-mineralogic framework. Reactive minerals, such as  $CaCO<sub>3</sub>$  (calcite), Fe(OH)<sub>3</sub>, clay minerals, and  $SiO<sub>2</sub>$  glass, and ion exchange-adsorption reactions are important in controlling groundwater composition for major solutes and some trace elements.

## **2.2.1 Previous Work**

The current conceptual hydrogeochemical model for the Pajarito Plateau is a synthesis of previous geochemical investigations conducted over the past several years and is summarized in Robinson et al. (2005, 88767). Characterization of site geochemistry has taken place over the past decade with investigations conducted on mesa tops and within canyon bottoms (Gallaher and Koch 2004, 88747;

Adams et al. 1995, 47192; Blake et al. 1995, 49931; Broxton and Eller 1995, 58207; Longmire et al. 1996, 54168; Longmire and Goff 2002, 75905). Concerns over the occurrence of, or potential for, groundwater contamination by waste-disposal practices at the Laboratory prompted annual monitoring (Laboratory Environmental Surveillance Program [ESP] reports) since the 1950s and additional hydrogeochemical studies (Longmire 2002, 72614; 2002, 72713; 2002, 72800; 2002, 73282; 2002, 73676; and 2005, 88510). Geochemical modeling studies have further contributed to an understanding of geochemical processes occurring in both shallow and deep, local and regional, unsaturated and saturated groundwater systems (Broxton et al. 2002, 76006; Keating et al. 1999, 88746).

#### **2.2.2 Elements of the Conceptual Hydrogeochemical Model**

This subsection summarizes different elements contributing to the geochemical conceptual model. The ten elements that follow represent the conceptual hydrogeochemical model that integrates geochemistry, hydrogeology, and contaminant transport. Geochemical processes occurring over time and space are implicit to this conceptual model. The elements include natural chemical compositions of groundwater, redox conditions, adsorption and precipitation reactions, residence time, chemical speciation, and colloids. Reactive minerals are considered to be most important for controlling groundwater composition and solute mobility.

*Geochemistry Element 1:* Because of geochemical processes, the **natural composition** of groundwater can vary within and between the alluvium, perched-intermediate zones, and the regional aquifer and along flow paths from recharge to discharge zones.

*Geochemistry Element 2:* **Residence times** of groundwater and chemical solutes (mass of water or solute/flux of water or solute) increase with depth and from west to east across the Pajarito Plateau. Accordingly, increasing concentrations of major ions and trace elements are observed along the flow paths in perched systems and the regional aquifer.

*Geochemistry Element 3:* **Reactive constituents**, consisting of CaCO3, Ca-smectite, Na-feldspar, amorphous  $SiO<sub>2</sub>$ , and  $Fe(OH)<sub>3</sub>$ , may control groundwater composition for the major solutes and selected trace elements, including iron and aluminum. These reactive minerals and solid phases approach equilibrium with groundwater when the residence time exceeds the reaction half time (amount of time required for 50% of reactant A to form product B with B not initially present).

*Geochemistry Element 4:* **Alluvial aquifer material** provides the largest reservoir for effluent-discharged constituents such as strontium-90, cesium-137, uranium, plutonium-238, plutonium-239/240, and americium-241 because the constituents readily adsorb onto clay and silt-sized particles coated with clay minerals and ferric (oxy)hydroxide.

*Geochemistry Element 5:* In general, **adsorption** of radionuclides and organic and inorganic species in the Bandelier Tuff decreases as follows: cesium-137 (highest sorption) = americium-241 > plutonium-238 = plutonium-239/240 > strontium-90 > uranium > nitrate = sulfate = chloride = perchlorate = trichloroethylene (TNT) = research department explosive (RDX) = tritium (lowest sorption). Adsorption affinities are based on experimental (Longmire et al. 1996, 56030) and field data (ESP 2000, 68661; ESP 2001, 71301). Adsorption capacities of sediments and aquifer material may change over time and location as a result of changes in solution speciation and mineralogy.

*Geochemistry Element 6:* **Activities** of adsorbing radionuclides and concentrations of inorganic species, which are Laboratory derived, generally decrease downgradient along the groundwater flow path.

*Geochemistry Element 7:* **Non- and weakly adsorbing constituents** (tritium, perchlorate, nitrate, chloride, fluoride, ([RDX, TNT], and uranium) can migrate from alluvial groundwater to perchedintermediate zones and to the regional water table.

*Geochemistry Element 8:* Adsorption processes generally dominate over **mineral precipitation** for removing metals and radionuclides from alluvial groundwater. However, in isolated cases where effluent discharges have changed major ion chemistry and pH, trace solutes such as strontium and barium may precipitate as  $SrCO<sub>3</sub>$  and  $BaSO<sub>4</sub>$  or coprecipitate as  $(Sr-Ba)SO<sub>4</sub>$  in alluvial groundwater.

*Geochemistry Element 9:* **Transport** of constituents in groundwater occurs as both dissolved solutes and as colloids. Colloids may include natural material (silica, clay minerals, organic matter, and ferric oxyhydroxide) and possibly solid phases associated with the treated Laboratory discharges.

*Geochemistry Element 10:* **Young ages**, a component of groundwater within perched zones in the Sierra de los Valles and the regional aquifer, is less than 60 yr old. This observation is based on measurable tritium considerably above 1 pCi/L (Broxton et al. 2001, 71252; Broxton et al. 2002, 76006; Longmire et al. 2001, 70103). The initial cosmogenic baseline for tritium is approximately 17 pCi/L (Clark and Fritz 1997, 59168); however, cosmogenic tritium has decayed to less than 1 pCi/L as water moved from the surface to the regional water table over several decades. Measurable concentrations of tritium in the regional aquifer above the cosmogenic baseline occur in Pueblo Canyon, Los Alamos Canyon, Sandia Canyon, Mortandad Canyon, Pajarito Canyon, and Cañon de Valle downgradient from release sites (ESP, 2001, 71301; Longmire 2002, 73282; Longmire 2002, 72800; Longmire 2002, 73676; Longmire 2002, 72614; Longmire 2005, 88510).

## **2.2.2.1 Hydrochemistry, Natural Distribution of Solutes, and Residence Times (Elements 1 and 2)**

This section describes physical and chemical characteristics of recharge and discharge zones and groundwater chemistry.

The temperature of the recharge water is generally less than 15 $\mathrm{^{\circ}C}$ , but with increasing depth, groundwaters in the perched-intermediate zones within the Cerros del Rio basalt and Puye Formation and regional aquifer are generally greater than  $15^{\circ}$ C, reflecting the geothermal gradient associated with heat flow beneath the Jemez Mountains.

Figure 2.2-1 shows the average concentrations of several analytes at the fifteen stations measured from 1996 to 2000. A recharge zone occurs within the Sierra de Los Valles, and a discharge zone occurs in White Rock Canyon. Groundwater in the recharge zone is characterized by a calcium-sodiumbicarbonate ionic composition with a specific conductance generally less than  $110 \mu S/cm$ . Concentrations of dissolved calcium, magnesium, sodium, chloride, and bicarbonate increase in groundwater from the Sierra de los Valles eastward toward the Rio Grande (Figure 2.2-1). Concentrations of dissolved iron and manganese are less than 0.5 and 0.05 parts per million (ppm), respectively, which also suggest overall oxidizing conditions within the recharge zone. Groundwater discharging from springs in this region is generally oxidizing because concentrations of chemical reductants, including hydrogen sulfide, methane, and ammonium are less than detection.

Concentrations of tritium vary in recharge water because of local and seasonal variations. Recharge water derived from precipitation near the Sierra de los Valles contains tritium (19 to 71 pCi/L), which decays to less than 3 pCi/L along groundwater flow paths within noncontaminated perched-intermediate zones and the regional aquifer beneath the Pajarito Plateau (Figure 2.2-1). Dilution of water containing tritium also occurs within the vadose zone and regional aquifer. Concentrations of tritium at Spring 9B,

discharging from the Cerros del Rio basalt in White Rock Canyon, are less than 0.40 pCi/L, which suggests that the age of this groundwater is greater than 60 yr.

Groundwaters within the three aquifer types contain silica as a major solute. Higher concentrations of dissolved silica occur within the volcanic-derived rocks than in the Santa Fe Group sediments.

Figure 2.2-2 shows average dissolved concentrations of several natural trace elements within alluvial and perched-intermediate groundwater and the regional aquifer. Average concentrations of natural arsenic and fluoride are the highest within the Cerros del Rio basalt (Spring 9B). Average concentrations of barium, boron, bromide, strontium, and uranium are the highest within the regional aquifer at La Mesita Spring. Background concentrations of dissolved uranium are typically less than 1 part per billion (ppb) in groundwater within volcanic rocks, sediments, and alluvium west of the Rio Grande. Average concentrations of dissolved natural uranium are 9.1 µg/L at La Mesita Spring, which is 300 times greater than that observed at alluvial well LAO-B (Figure 2.2-2). Variations in trace-element concentration depend on solute residence time and the extent of water-rock interactions. Older groundwater within the regional aquifer tends to have higher concentrations of trace elements as a result of desorption processes.

Concentrations of trace elements within the three aquifer types are controlled by speciation (the form and structure of solute), oxidation state, and their affinity to adsorb onto aquifer material. Figure 2.2-3 shows calculated speciation of dissolved uranium(VI) at Spring 9B, in which uranyl dicarbonate dominates between pH values 6.6 and 8.4. Barium and strontium are predicted to occur as  $Ba^{2+}$  and  $Sr^{2+}$  and undergo cation exchange reactions. Boron is stable as the hydrolysis species B(OH)<sub>3</sub><sup>0</sup>, and this neutrally charged solute does not adsorb onto aquifer material, making it an excellent tracer or nonreactive species. Fluoride and bromide are stable as F<sup>-</sup> and Br<sup>-</sup>, respectively, and these two anions are also excellent tracers. Other trace elements, including copper (II), form complexes with carbonate and sulfate, making them less adsorptive than the noncomplexed forms.

Trace-element concentrations and major ion ratios in the regional aquifer beneath the Pajarito Plateau are dramatically different from waters sampled in the western Valles Caldera region (Shevenell et al. 1987, 06673; Blake et al. 1995, 49931). Therefore, it can be concluded that the western half of the Valles Caldera is not a plausible recharge area for the regional aquifer beneath the Pajarito Plateau. Water samples collected in the western portion of the Sierra de los Valles, although sparse, are geochemically similar to Pajarito Plateau perched groundwater and the regional aquifer (Robinson et al. 2005, 88767; thus, this region cannot be excluded from the potential recharge area based on geochemical evidence alone.

Isotopic data ( $\delta^{18}$ O and  $\delta$ D ratios) from cold springs discharging from the regional aquifer (Vuataz and Goff 1986, 73687; Blake et al. 1995, 49931; Longmire 2002, 72614; 2002, 72713; 2005, 88510) may be used to distinguish between recharge in the Valles Caldera, Sierra de los Valles, and possibly the Sangre de Cristo mountains (for well samples near the Rio Grande). Paleotemperatures of colder climate indicative of the Pleistocene produce lighter  $\delta$ D and  $\delta^{18}$ O values (Clark and Fritz 1997, 59168); temperature effects need to be considered in evaluating samples collected from deep wells in lower Los Alamos Canyon and within San Ildefonso Pueblo. Available isotopic data do not support a hydrologic connection between the regional aquifer beneath the Pajarito Plateau and the Valles Caldera.

The most likely source of recharge for the western part of the Pajarito Plateau occurs within the Sierra de los Valles. Major ion compositions of Apache Spring, upper Cañon de Valle Spring, surface water in both upper Cañon de Valle and Water Canyon, and the perched-intermediate zone observed at wells R-18, R-25, and R-26 are very similar (calcium-sodium-bicarbonate ionic composition), suggesting common host rocks and a common recharge zone.

Residence times of groundwater and chemical solutes increase both with depth and from west to east across the Pajarito Plateau (Figure 2.2-1). Accordingly, increasing concentrations of major ions and trace elements are observed along the flow paths, but concentrations of tritium tend to decrease with depth. Residence times of the recharge groundwater may be short, based on the open fracture flow within the Bandelier Tuff, Tschicoma Formation, and Cerros del Rio basalt and within porous media flow in the coarse-grained alluvium in upper Los Alamos Canyon and other canyons. Increasing residence times occur within perched-intermediate zones and in the regional aquifer. A recent component of groundwater, based on tritium observed within the perched zones and/or at the regional water table is observed at wells R-4, R-5, R-6, R-6i, R-8, R-9, R-9i, R-11, R-12, R-15, R-22, R-23, R-25, R-28, and MCOBT-4.4. Tritium has been measured at these wells at concentrations above the initial cosmogenic baseline.

## **2.2.2.2 Reactive Minerals (Element 3)**

Geochemically reactive minerals and amorphous solids react with groundwater along flow paths to varying degrees. These solids approach equilibrium with groundwater when the residence time exceeds the reaction half time. These reactive constituents, consisting of calcite (CaCO<sub>3</sub>), Na-feldspar, Ca-smectite, amorphous  $SiO<sub>2</sub>$ , and Fe(OH)<sub>3</sub>, may control groundwater composition for the major ions and selected trace elements, including iron and aluminum. Reactive minerals have varying adsorption capacities for trace elements, including arsenic, chromium, nickel, lead, selenium, and uranium. Each of the major reactive constituents along flow paths beneath the Pajarito Plateau is discussed below.

*Calcite*: Concentrations of dissolved calcium and bicarbonate increase in depth within perchedintermediate zones and the regional aquifer (Longmire 2002, 72713; 2002, 72800; 2002, 73282; ESP 2000, 68661; ESP 2001, 71301), reflecting the increase in residence times within the deeper saturated zones. Figure 2.2-4 shows saturation indices for calcite versus calcium and bicarbonate concentrations (millimoles/liter) at background springs and wells. The saturation index (SI) is defined as the log10(activity product/solubility product). The computer program MINTEQA2 (Allison et al. 1991, 49930) was used to perform SI calculations. For a given solid phase at equilibrium, saturation is equal to 0 ± 0.05. Oversaturation (positive SI) implies precipitation, but undersaturation (negative SI) implies dissolution. Alluvial and perched-intermediate groundwaters are calculated to be undersaturated with respect to calcite, and dissolution of this mineral takes place. This calculation is consistent with the absence of calcite within the saturated alluvium upgradient from the Laboratory. Calcite is an important reactive mineral controlling dissolved concentrations of calcium and bicarbonate in the regional aquifer. The regional aquifer (Santa Fe Group sediments and basalt) is calculated to be in close equilibrium with respect to calcite. Groundwater samples collected at wells R-9, R-12, and Otowi-4 and La Mesita Spring generally are saturated with respect to calcite, whereas the perched-intermediate well LAOI(A)-1.1 is not. Activities of dissolved calcium and bicarbonate at well LAOI(A)-1.1 are not sufficient enough to allow for calcite precipitation. Calcite typically is not observed in native groundwater within the alluvium and Bandelier Tuff.

*Smectite*: Extensive zones of smectite were encountered in the Puye Formation in core and cutting samples collected from R-9 and R-12 (Broxton et al. 2001, 71250; 2001, 71252). Smectite has also been observed in rock samples collected from the Santa Fe Group sediments in lower Los Alamos Canyon. Figure 2.2-5 shows log activity H<sub>4</sub>SiO<sub>4</sub> (silicic acid) versus log activity Ca<sup>2+</sup>/[H<sup>+</sup>]<sup>2</sup> at 25°C for wells R-9, Otowi-4, R-12 (screen #3), and LAOI(A)-1.1 and La Mesita Spring. Groundwater samples collected from these stations dominantly plot within the stability field of calcium smectite, suggesting that most groundwater is oversaturated with respect to this mineral. One sample collected from La Mesita Spring, however, plots within the stability field for kaolinite, because of the more acidic pH measured during the sampling round. Smectite increases the adsorption capacity of the aquifer material for cations (metals and radionuclides) under circumneutral pH conditions.

*Silica*: Silica glass derived from volcanic rocks is an important component of the Bandelier Tuff, pumicerich zones of the Puye Formation, and Cerros del Rio basalt. Groundwater (alluvial, perchedintermediate, and regional aquifer) reacting with silica glass produces dissolved silica, in the form of silicic acid [Si(OH)4]. Concentrations of dissolved silica vary as a function of the solubility of silica glass containing sodium, potassium, and calcium (Lindsay 1979, 00883). Groundwaters collected from selected wells and springs are oversaturated with respect to silica-rich soil and undersaturated with respect to  $SiO<sub>2</sub>$ glass (Figure 2.2-5). These groundwaters are also oversaturated with respect to quartz, cristobalite, and tridymite based on thermochemical data provided by Lindsay (1979, 00883). These  $SiO<sub>2</sub>$  phases are present within the Guaje Pumice Bed, as identified in core collected from borehole LAOI(A)-1.1. La Mesita Spring is undersaturated with respect to silica-rich soil and silica glass because of lower concentrations of silica relative to those measured in groundwater samples collected at wells R-9, Otowi-4, R-12, and LAOI(A)-1.1.

*Na-feldspar*: Sodium-rich feldspar (albite) is present in the Santa Fe Group sediments, and over thousands of years this phase has reacted with groundwater, releasing sodium and silica to solution under basic pH conditions. The mineral chemically alters to form clay minerals, including kaolinite and sodium-rich smectite (Langmuir 1997, 56037), although volcanic-derived silica glass is more reactive.

*Fe(OH)3*: Hydrous ferric oxide (HFO) is ubiquitously found in hydrogeologic environments and is an important adsorbent for many trace elements, including arsenic, chromium, lead, and uranium. This phase has a specific surface area of 600 m<sup>2</sup>/g (Langmuir 1997, 56037) that contributes to its high adsorptive capacity. HFO has been observed as a component of fracture-fill material at borehole R-9 within the Cerros del Rio basalt (Broxton et al. 2001, 71250). Chemical and mineralogical data collected from the borehole indicate that uranium is associated with HFO and smectite within the fracture-filling material. Oxidation-reduction reactions are also controlled by HFO and dissolved ferrous iron (Langmuir 1997, 56037) under acidic to neutral pH conditions. In addition to HFO, hydrous manganese oxide (HMO) is an important adsorbent within volcanic and sedimentary rocks. This phase is found at lower concentrations than HFO, based on elemental analysis of core samples and nonfiltered water samples containing suspended particles.

## **2.2.2.3 Contaminant Distributions and Transport (Elements 4 through 10)**

Background distributions of chemicals in groundwater have direct relevance to defining the nature and extent of contamination. Geochemical processes controlling distributions of background solutes also occur in contaminated groundwater.

The largest mass distribution of adsorbing contaminants in Los Alamos Canyon and Mortandad Canyon occurs within the alluvium (Laboratory ESP reports). Alluvial groundwater in both Los Alamos Canyon and Mortandad Canyon contains elevated concentrations of strontium-90, cesium-137, uranium, plutonium-238, plutonium-239/240, and americium-241. This observation supports the concept that most of these radionuclides, except uranium and tritium, significantly adsorb onto aquifer material. Concentrations of adsorbing radionuclides and cationic metals generally decrease downgradient along the groundwater flow path. One or more of the nonadsorbing contaminants (tritium, perchlorate, chloride, nitrate, uranium, RDX, and/or TNT) has been observed at wells Otowi-1, MCOBT-4.4, R-4, R-5, R-6, R-6i, R-8, R-9, R-9i, R-11, R-12, R-15, R-25, and R-28.

The presence of colloids may enhance the movement of contaminants, especially those that are adsorbed onto fine-grained particles in the shallow subsurface. Colloid transport in alluvial groundwater has been documented in Mortandad Canyon (Penrose et al. 1990, 11770). The sources of colloids probably include natural materials (clay minerals, silica glass, ferric (oxy)hydroxide, and solid organic

matter) and possibly solid phases (silica glass and calcium carbonate) associated with the treated Technical Area 50 (TA-50) discharge. These colloids partly influence the distribution of suspended radionuclides within alluvial groundwater in Mortandad Canyon because constituents adsorbed onto colloids are transported more rapidly than they would be transported as dissolved solutes.

## **2.2.2.4 Cerro Grande Fire**

The Cerro Grande fire of May 2000 perturbed surface water and alluvial groundwater chemistry (Gallaher and Koch 2004, 88747; Katzman et al. 2000, 69055; Longmire et al. 2001, 70103). Ash produced from the fire has been transported within canyon systems reacting with rain and surface water. Increasing concentrations of total organic carbon (TOC) and DOC, carbonate alkalinity, calcium, potassium, iron, manganese, and other solutes occurred in surface water and alluvial groundwater for a few years (2000 to 2003) following the Cerro Grande fire (Gallaher and Koch 2004, 88747). In most canyons, carbonate alkalinity in surface water increased by factors of three to six after the fire. Surface water and alluvial groundwater showed increases in turbidity from ash and enhanced erosion.

Storm events remobilized contaminated sediments, and desorption of contaminants took place, resulting in a redistribution of contaminants for several years (Gallaher and Koch 2004, 88747). Cation exchange reactions involving strontium-90 and calcium and complexation reactions of uranium and bicarbonate are examples of hypothesized geochemical processes occurring in surface water and alluvial groundwater since the fire. On the whole, metal, radionuclide, and anion concentrations have decreased and are approaching pre-Cerro Grande fire concentrations in alluvial groundwater.

Oxidation and reduction reactions occurring between organic-rich ash and metals and radionuclides influence aqueous speciation of solutes and adsorption processes. It is hypothesized that DOC produced from the fire serves as an electron donor (reducing agent) during complete oxidation to bicarbonate and carbonic acid. Concurrently, iron(III) and manganese(IV) solids become electron acceptors (oxidizing agents) and are reduced to more soluble aqueous species. Geochemical data collected in Pueblo Canyon, Los Alamos Canyon, and Pajarito Canyon support the occurrence of these oxidation-reduction reactions with respect to DOC and dissolved iron and manganese (Gallaher and Koch 2004, 88747).

## **2.2.2.5 Summary of Geochemical Conceptual Model**

The preceding hydrogeochemical conceptual model applies to both background and Laboratory-induced conditions. This model addresses recharge and discharge zones, geochemical reactions, residence times, reaction half times, and temporal and spatial relationships.

Stable isotope ratios ( $\delta$ D and  $\delta^{18}$ O) strongly suggest that the Sierra de los Valles provides most of the recharge to groundwater beneath the Pajarito Plateau. This finding is based on similarities in isotopic ratios between springs discharging within the Sierra de los Valles and perched-intermediate groundwater and the regional aquifer beneath the Plateau. Recharge from the Valles Caldera to deep groundwater beneath the Pajarito Plateau is not significant. Additional recharge to the regional aquifer occurs along wet canyon bottoms on the Pajarito Plateau.

Measurable activities of tritium observed in springs discharging within the Sierra de los Valles (>10 pCi/L) suggest that a component of groundwater is less than 60 yr old within this recharge zone. Most of the springs discharging within White Rock Canyon, however, do not contain tritium, and the age of groundwater probably ranges between 3000 and 10,000 yr (Vuataz and Goff 1986, 73687).

Major ion chemistry of the regional aquifer varies from west to east across the Pajarito Plateau, from a calcium-sodium-bicarbonate to a sodium-calcium-bicarbonate ionic composition. Most notably, calcite

precipitation is observed in regional aquifer groundwater east of the Pajarito Plateau in wells near the Rio Grande. This finding is notable because of higher carbonate and bicarbonate concentrations in groundwaters at the eastern part of the Laboratory that enhance the precipitation of calcite. Total dissolved solids (TDS) generally increase along groundwater flow paths in the alluvium, perchedintermediate zones, and the regional aquifer.

Concentrations of trace elements increase from alluvial groundwater to perched-intermediate zones to the regional aquifer. They also increase from west to east within the regional aquifer as a result of increasing solute residence times and water/rock interactions. Concentrations of natural dissolved uranium are the highest within the regional aquifer, ranging from 0.5  $\mu$ g/L at Los Alamos to over 1800  $\mu$ g/L east of the Rio Grande.

## **3.0 SCOPE OF ACTIVITIES AND METHODS**

## **3.1 Data-Quality Objectives**

Before conducting this investigation, the Laboratory used the EPA data-quality objective (DQO) process (EPA 1987, 57589; 1992, 54947; and 1994, 48639), a strategic planning approach for a data collection activity. By using the DQO process, the Laboratory has ensured that the type, quantity, and quality of background hydrogeochemical data and information used in the decision-making process will be appropriate to meet the objective of determining natural background concentrations of inorganic and organic solutes and radionuclides in groundwater.

The DQO process used in this investigation consisted of seven steps, which are described below. The output from each step influences the choices that will be made in the next steps of the DQO process. This process is iterative; therefore, the outputs from one step may lead to reconsideration of previous steps. The DQO process consists of the following: (1) problem definition, (2) data evaluation or decision criteria, (3) data input for the different aquifer types, (4) spatial and temporal boundaries for sample stations, (5) decision rules, (6) uncertainty (statistical testing), and (7) design optimization.

#### **3.1.1 Problem Definition**

Adequate data to represent the distribution of solutes and total (suspended and dissolved fractions) concentrations in groundwater that represent background (or pre-Laboratory-induced) conditions are generally lacking before 1997. The ability to distinguish between natural and Laboratory-impacted conditions is essential for assessing data collected during site investigations, establishing cleanup levels, and understanding hydrologic and geochemical processes.

Although the Laboratory, U.S. Geological Survey, DOE, University of New Mexico, and consulting companies have published hydrogeochemical data collected before 1997, there are problems with using these data to represent background groundwater conditions because of issues with consistency. For example, many of the groundwater samples collected by the Laboratory were not filtered before analyses. Subsequently, analytical accuracy and precision vary from sample to sample, depending on the amount of suspended solids.

In 1997, groundwater-quality databases were reviewed in terms of sample collection and preservation, chemistry, hydrogeology, time of sample collection, and completeness and accuracy of reported analytical results. From this evaluation, both analytical and data gaps were identified. Different sample preparation and analytical techniques had been used. Thus, groundwater-quality data collected under different Laboratory programs generally were not directly comparable. Background subsurface databases
provided for the former Environmental Restoration (ER) Project before 1997 were generally internally consistent in terms of sample collection, filtering, field preservation, selection of analytes, analytical methods, and precision and accuracy.

Statistical analyses of the pre-1997 groundwater background data considered issues relating to data quality and exploratory data analysis of various sample locations. Only filtered data were evaluated because nonfiltered samples are known to have a positive bias for inorganic chemicals typically found in suspended sediments. High-quality data for major ions are evidenced in the pre-1997 data by the close agreement in the calculated charge balance of anions and cations. In addition, variability of the measurement process through laboratory duplicate samples was measured at  $\pm 20\%$  (with one outlier value excluded). The analysis of the pre-1997 samples showed variability between aquifer types (alluvial, perched-intermediate, and the regional aquifer) with concentrations of bicarbonate and TDS being greatest in groundwater samples collected from the regional aquifer (Santa Fe Group and Puye Formation). However, the nonuniform sample intervals and timing of sampling events between locations hinder the use of the pre-1997 data as possible background sample locations. Appendix D provides additional information on geochemical and statistical analyses using the pre-1997 hydrogeochemical data.

Numerous nonfiltered groundwater samples have been collected and analyzed for inorganic chemicals and radionuclides. Analytical results for these samples are not useful because the nonfiltered samples contained suspended particles. When the turbid water samples are acidified with nitric acid at a pH of 2, suspended particles consisting of clay minerals, ferric (oxy)hydroxide, manganese oxide, calcium carbonate, and feldspar partially or completely dissolve. This dissolution results in elevated concentrations of major ions (calcium, magnesium, potassium, and sodium) and trace elements (aluminum, iron, barium, beryllium, manganese, and uranium), which produce false positives in analytical results.

Because of the limited number of background wells completed in the alluvium, Bandelier Tuff, Cerros del Rio basalt, and Puye Formation, background hydrogeochemical data available up to 1997 do not include the full range of natural concentrations for all analytes of environmental concern. Before 1994, very limited background hydrogeochemical data were available for alluvial (well LAO-B) and perchedintermediate aquifers (well LAOI(A)-1.1 and well R-7 [screen #1]). Limited hydrogeochemical data (filtered samples) were collected from selected springs that discharge from the Cerros del Rio basalt (Spring 9B) and hydro (phreatic)-magmatic deposits (Doe Spring) within White Rock Canyon.

For the above reasons, the decision was made in 1997 to establish background hydrogeochemical data sets using wells and springs that are representative of various groundwater bodies along flow paths beneath the Pajarito Plateau.

# **3.1.2 Data Evaluation Criteria**

If analytical results for both filtered and nonfiltered groundwater samples, with turbidity values of less than five nephalometric turbidity units (NTUs), are considered to be free from Laboratory influence and meet the data assessment criteria, then those groundwater data will be considered representative of background conditions. The Laboratory uses quantitative and qualitative approaches to data evaluation, which are supported by statistical analyses and geochemical evaluation. Statistical analyses include outlier assessments and distribution analysis. Geochemical evaluation of the background data includes comparing cation-anion distributions; determining the presence or absence of tritium in relation to recharge and discharge zones; observing the absence of specific Laboratory-derived contaminants,

including chlorate, perchlorate, and nitrate; evaluating trace-element geochemistry; and measuring stable isotope ratios of hydrogen, nitrogen, and oxygen.

### **3.1.3 Data Inputs**

The hydrogeologic conceptual model for groundwater beneath the Pajarito Plateau (see Section 2.1.5) indicates that groundwater occurs in three modes: alluvial, perched-intermediate, and the regional aquifer. The groundwater chemistry within each mode varies because of differences in aquifer mineralogy (reactive phases controlling water composition), hydrogeochemical processes, including adsorption/desorption and mineral precipitation/dissolution reactions, source(s) of water, and residence time of groundwater and solutes (Section 2.2). Variations in groundwater temperature are also observed among the three aquifer types, where increasing temperature is observed with depth. Therefore, establishing background conditions requires the data inputs for each mode of groundwater provided in Table 3.1-1. Names and locations of background stations are provided in Table 3.1-2.

### **3.1.4 Spatial and Temporal Boundaries**

Available groundwater-quality data were compiled, and the following specific criteria were applied to identify groundwater beneath the Pajarito Plateau that is not affected by Laboratory operations:

- greater than 60 yr old, based on the activity of tritium, except for alluvial groundwater upgradient from the Laboratory and springs discharging within Sierra de los Valles or within other recharge zones,
- located hydrologically upgradient from the Laboratory or downgradient in areas not containing Laboratory-derived contaminants, and
- generally known mode of groundwater occurrence (alluvial groundwater, perched-intermediate zones, and regional aquifer).

Groundwater quality at two alluvial sampling stations (Pine Spring and well LAO-B) may vary on a seasonal basis, particularly during seasons with greater precipitation that provide input to the hydrologic system. Hydrogeochemical data consist of verified analytical results from both filtered and nonfiltered samples collected on a quarterly basis over a period of 1 to 1.5 yr (6 rounds of sampling). Evaluation of the historical water-quality data suggests that the variability of major ions and trace solutes was greatest in alluvial groundwater because of chemical variability over time with recent recharge from surface water.

#### **3.1.5 Decision Rules**

If analytical results for groundwater samples collected from a single mode of groundwater occurrence meet the data assessment criteria, then these data will be included in statistical analyses to establish background distributions for each analyte for that mode of groundwater occurrence.

Steps in the data assessment are as follows:

- Evaluate the sample analytical results for each analyte to determine the overall variability and to verify the hypothesized differences between water sources (alluvial, perched-intermediate, and regional aquifer).
- Within a statistical population, determine if there are any outliers.
- Perform a regression analysis. Standardized residuals from regression analysis of milliequivalent total anions versus milliequivalent total cations for filtered samples should not be greater than  $± 5%$ .
- Assess variability. Variability from laboratory analyses should be small compared to temporal/spatial variability of groundwater samples; a target value is to have less than 25% relative standard deviations from laboratory duplicates.

### **3.1.6 Uncertainty**

Statistical testing is based on a nominal 5% significance level of a 95% confidence level. The power of these tests to detect variability depends largely on the seasonal variation measured at the background sample locations.

### **3.1.7 Design Optimization**

Because groundwater sample locations for background must be defined (i.e., locations must be credible upgradient or in unimpacted areas), a statistical design optimization is not practical. Rather, the available locations were evaluated and selected using expert judgment to encompass geographic and hydrological variation.

Based on the spatial boundary criteria listed in Section 3.1.4, 14 of the 15 sampling stations (excluding Pajarito Spring) represent locations whose groundwater is hypothesized to be unaffected by Laboratory operations (Table 3.1-2). Pajarito Spring was separated from the other sites because of the occurrence of perchlorate and nitrate, based in part on data collected at the spring after 2000. Information on the geologic and hydrologic system at the Laboratory (see Section 2.0) was used to categorize background sampling sites as part of an alluvial system, an intermediate-depth perched system, or a deep regional system (Table 3.1-2). Different criteria were used for the assignment of waters from these sites, depending on whether they came from wells or springs.

Classification of groundwater was based on (1) well depth, (2) hydrogeologic units penetrated, (3) depth to the zone of saturation sampled and observed, or (4) the projected position of the regional water table at that location. Groundwater collected from well LAO-B was considered to be perched in the alluvium because it was the only well penetrating the alluvium upgradient of the Laboratory boundary. Water from well LAOI(A)-1.1 (Guaje Pumice Bed) was assigned to the intermediate-depth perched system because the saturated zone from which it came lies above the projected position of the regional water table. Groundwater samples collected from supply wells Otowi-4 and Guaje-5 were classified as regional groundwater because those wells are only screened in the deep groundwater system.

Classification of spring waters is more difficult because of a lack of subsurface data and information. Several criteria were applied in classification: position relative to the regional water table, geologic material at the spring outlet, hydrologic conditions in the area, height relative to the Rio Grande, and water chemistry. Several springs are within recharge boundaries in the Sierra de los Valles (Water Canyon Gallery, Pine Spring [alluvium], Apache Spring, and upper Cañon de Valle Spring). This hydrologic setting indicates that these groundwaters had relatively short travel or residence times within the volcanic rocks and alluvium. Several springs in White Rock Canyon discharge from the Cerros del Rio basalt (Spring 9B) and from hydromagmatic deposits (Doe Spring) and were assigned to the regional aquifer. Some spring waters discharging from elevations slightly above that of the Rio Grande were also assigned to the regional groundwater system. These springs occur in an area of known artesian conditions and had low tritium activity, suggesting that they have had a long travel time (Sacred Spring, Spring 1, and La Mesita Spring). Pajarito Spring (Spring 4A) discharges from Totavi gravels overlain by

slump blocks consisting of Cerros del Rio basalt. Pajarito Spring is considered part of the regional aquifer system. Chemical data collected from Pajarito Spring were not combined with the other springs because nitrate and perchlorate were present. These two tracers are found at lower (background level) concentrations at Doe Spring and Spring 9B.

Although the position of the groundwater divide west of the Laboratory is uncertain, Seven Springs clearly lies west of the divide. Nonetheless, it is included here because it discharges from the Bandelier Tuff and its major ion chemistry is similar to that of well LAOI(A)-1.1. Similarly, La Mesita Spring is also included in this study for geochemical comparison purposes, even though it is located east of the Rio Grande and is not part of the hydrologic system associated with the Pajarito Plateau. Chemical data collected at La Mesita Spring, however, were not combined with the other springs for statistical analyses of the background distribution of chemicals. La Mesita Spring is a stand-alone sampling station with respect to statistical analyses.

The sampling design included an analysis of groundwater samples to characterize both inorganic constituents and radionuclides. Primary inorganic constituents of concern (anions) found in groundwater at the Laboratory include nitrate, chloride, perchlorate, sulfate, and fluoride. Radionuclides observed in groundwater at the Laboratory consist mainly of tritium, strontium-90, cesium-137, uranium-234, uranium-235, uranium-238, plutonium-238, plutonium-239/240, and americium-241. Background level distributions of these anions and radionuclides were determined by sampling:

- springs that discharge east, west, and north of the Laboratory boundary and east of the Rio Grande;
- upgradient characterization/monitoring wells installed by the former ER Project;
- supply wells, characterization wells, and springs that contain concentrations of anions less than those observed in contaminated groundwater; and
- supply wells, characterization wells, and springs downgradient of Laboratory releases that contain concentrations of tritium less than 1 pCi/L and/or activities of fallout-derived radionuclides (strontium-90, cesium-137, plutonium-238, plutonium-239/240, and americium-241) less than detection, except for naturally occurring uranium isotopes.

#### **3.2 Field and Laboratory Analytical Methods**

Over the course of this investigation, both the field instrumentation used and the types of groundwater samples collected for chemical analyses varied. From 1997 to 2000, six sampling rounds were completed. Results of field measurements taken at the sampling stations are provided in Table 3.2-1. Most of the groundwater samples were collected in 1997, 1998, and 2000; only a few additional samples were collected in late 1999. During 1998 and early 2000, supply well Guaje-5 was not available for sampling because the well was taken offline for pump repair; in 2000, supply well Otowi-4 was not available for sampling for the same reason. The following laboratories collected groundwater samples for chemical and radiochemical analyses:

- Los Alamos National Laboratory's Earth and Environmental Sciences-6 (EES-6) geochemistry laboratory for general aqueous geochemistry (1997 through early 2000, five sampling rounds);
- University of Miami for low-level tritium analyses (1997 through 2000, six sampling rounds);
- Teledyne for tritium analyses (1998, two sampling rounds);
- Paragon Analytics, Inc., for radionuclides using both different analytes and different methods (1997 through 1998, three sampling rounds) and general aqueous geochemistry analyses (1998 through 2000, four sampling rounds);
- Huffman Laboratory for DOC fractionation analyses (1997 through 1998, three sampling rounds);
- Western Michigan University for stable isotope analyses of  $\delta$ D and  $\delta^{18}$ O (1997 through 1998, four sampling rounds);
- Geochron Laboratory for stable isotope analyses of  $\delta$ D and  $\delta^{18}$ O (1999 through 2000, two sampling rounds);
- General Engineering Laboratories (GEL) for selected trace elements (1999 through 2000, two sampling rounds); and
- Coastal Sciences Laboratory for  $\delta^{15}N$  isotopes (late 1998 to 2000, two sampling rounds).

#### **3.2.1 Field Methods**

In general, most groundwater samples were collected in plastic bottles. Samples collected for stable isotope and DOC fractionation analyses were collected in clear and brown glass bottles, respectively. Samples for DOC fractionation were filtered through 0.45  $\mu$ m silver filters to inhibit microbial degradation of organic carbon. Other filtered samples were processed using  $0.45 \mu m$  acetate filter membranes. Before 1998, a hand-operated vacuum pump was used to filter groundwater samples. The samples were filtered on-site immediately following collection or within 6 hr of the collection time. In 1998 and subsequent sampling rounds, the field team used a battery-operated vacuum pump to filter the water. A sample duplicate was collected in the field for every five primary samples. The field duplicate samples were separate aliquots collected during the same sampling event for a location. Total carbonate alkalinity was determined in the laboratory using standard titration techniques within 48 hr of sample collection.

Groundwater samples were either preserved with ice at  $4^{\circ}$ C or using concentrated HNO<sub>3</sub> or concentrated H<sub>2</sub>SO<sub>4</sub>. The pH of acidified samples (metals, nitrogen isotopes, nitrate plus nitrite, and radionuclides excluding tritium) was lowered by the drop-wise addition of acid to a pH of <2. Care was taken to avoid the trapping of air in the nonacidified samples.

The field parameters recorded for each of the fifteen sampling stations included pH, temperature (°C), specific conductance  $(\mu S/cm)$ , and turbidity (NTU). Appendix A provides the field-measured parameters taken at each sampling station and the sampling dates. In 1997, a Horiba meter was used to determine pH, conductivity, and turbidity. The meter was calibrated daily, according to manufacturer specifications, using Autocal solution. Temperatures were measured using a Fluke 52 K/J thermometer and probe.

After 1997 the field instrumentation changed. For the remainder of the investigation, an Orion temperature-compensated pH meter was used for temperature and pH. The meter was calibrated daily using three buffer solutions ( $pH = 4.01$ , 7.00, and 10.01). Specific conductance was measured with two Hanna temperature-compensated conductivity meters. The meters were calibrated at the beginning of the field season. The calibration was rechecked, and if necessary, corrected during the field season if discrepancies between the two meters occurred. Turbidity was measured with a Hach turbidmeter calibrated at the beginning of the field season. Over the course of the study, pH for a few samples was measured using limited-range pH indicator strips.

The Orion meter has a resolution of 0.01, and accuracy is reported as  $\pm$ 0.01 for pH. Temperature resolution and accuracy are 0.1°C and ±1.0°C, respectively. The Hanna conductivity meters have a resolution of 10 µS/cm, and accuracy is reported as ±40 µS/cm. The Hach turbidmeter has a resolution of 0.1 NTU below 100 NTU and an accuracy of ≤5% of the reading or ±0.1 NTU, whichever is greater.

Water samples at springs were generally collected through a funnel-tubing system that allowed for minimal disturbance of the bottom sediments. The funnel was placed in the spring, and the tubing was extended downhill. Sufficient time was allotted to allow the bottom sediments in the spring to settle and for the apparatus to be rinsed. The sample water was then collected from the end of the tubing. In some locations the spring consists of a deep basin with a seep-like outflow. These waters were collected by dipping a beaker into the pool, or in later samples, by pumping the water directly from the spring to the sample container. Except for turbidity measurements with the Hach meter, field parameters were collected by placing the individual meters directly into the pool of spring water. Samples collected for turbidity measurements using the Hach meter were dipped from the pool of water and were placed into a sample measurement cell.

Groundwater samples collected from supply wells Guaje-5 and Otowi-4 were collected from a spigot or from tubing connected in line with the pump. Groundwater pumped from the supply wells was collected after running the water for five minutes. Groundwater from wells LAO-B and LAOI(A)-1.1 was collected after removing at least three well volumes of groundwater to determine the field parameters had stabilized. At these wells, the field parameters were measured at 5-gal. intervals. Field parameters for all the wells were measured in a bucket filled with the well water.

## **3.2.2 Analytical Methods**

**Paragon Analytics**, **Inc.**, also analyzed groundwater samples collected as part of this investigation. Paragon used standard techniques specified by the U.S. Geological Survey (USGS 1989, 88749), the American Public Health Association (American Public Health Association 1985, 88769), the Annual Book of ASTM Standards (ASTM 1988, 68413), and EPA method SW-846 (EPA 1987, 31732). Ion chromatography (IC) was the method used by Paragon to determine concentrations of bromide, chloride, fluoride, oxalate, nitrate, nitrite, phosphate, and sulfate in the water samples. Concentrations of aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, strontium, thallium, vanadium, and zinc were determined by inductively coupled plasma atomic (optical) emission spectroscopy (ICPAES). Colorimetry was used to analyze for total cyanide. Cold-vapor atomic absorption (CVAA) was used to analyze for mercury. Inductively coupled plasma mass spectrometry (ICPMS) was used to analyze for antimony, beryllium, cadmium, lead, thallium, and uranium for two sampling rounds (December 1999 and January 2000, and March and April 2000).

Paragon Analytics, Inc. performed radiochemical analyses on water samples. The methods used included laser-induced kinetic phosphorimetric analysis (LIKPA) for uranium; alpha spectrometry for americium-241, plutonium-238, plutonium-239/240, uranium-234, uranium-235, and uranium-238; gamma spectrometry for cesium-137, and other gamma-emitting isotopes; and gas proportional counting for strontium-90.

**GEL** analyzed groundwater samples collected in late 1999 and 2000 for antimony, beryllium, cadmium, lead, thallium, and uranium using ICPMS. Detection limits for these analytes generally range from 0.1 to  $0.5 \mu g/L$ .

**Huffman Laboratories** performed DOC fractionation analyses using an in-house, EPA-modified method based on physical separation. This method consists of separating hydrophilic (acid, base, and neutral groups) from hydrophobic functional groups (acid, base, and neutral groups). This analysis method

provides information on the distribution of naturally occurring organic compounds, including fulvic and humic acids (hydrophobic groups) and small molecular-weight organic compounds (hydrophilic groups).

Groundwater samples were also analyzed for inorganic chemicals at **EES-6** using additional techniques specified in EPA SW-846 (EPA 1987, 31732). Ion chromatography was used for determining concentrations of bromide, chloride, fluoride, nitrate, nitrite, oxalate, phosphate, and sulfate. EES-6 used graphite furnace atomic absorption (GFAA) in determining concentrations of cadmium, cesium, chromium, cobalt, copper, lead, molybdenum, nickel, rubidium, silver, thallium, and tin in the groundwater samples. Hydride atomic absorption (HAA) was used for measuring arsenic, antimony, and selenium concentrations in the samples. Mercury analysis was done by the CVAA method. ICPAES was the method used for determining concentrations of aluminum, barium, beryllium, boron, calcium, iron, lithium, magnesium, manganese, potassium, silicon, sodium, strontium, titanium, vanadium, and zinc in the groundwater samples. An ion-specific electrode (ISE) was used to measure ammonium concentrations in the samples.

The **University of Miami** performed tritium analyses using direct counting for tritium and electrolytic enrichment for low-level tritium (less than 3.2 pCi/L) . **Teledyne** performed tritium analyses using direct counting and/or liquid scintillation (300 pCi/L).

Stable isotopes of oxygen (oxygen-18 and oxygen-16,  $\delta^{18}O$ ) and hydrogen (deuterium and hydrogen,  $\delta D$ ) were analyzed by **Western Michigan University** (WMU) and **Geochron Laboratories,** Cambridge, Massachusetts, using isotope ratio mass spectrometry (IRMS). Stable isotopes of nitrogen (nitrogen-15 and nitrogen-14, δ<sup>15</sup>N) were analyzed at **Coastal Sciences Laboratories, Inc.**, Austin, Texas.

# **3.2.3 Analytes of Interest**

Field parameters, major ions, neutral species, trace elements, DOC fractionation, stable isotopes, and radionuclides measured or analyzed as part of this investigation are provided in Table 3.2-2.

# **3.3 Scope of Groundwater Background Investigations in Time and Space**

This subsection presents an overview of the fifteen sampling stations selected for the groundwater background investigations from 1997 to 2000. More detailed information is provided in Appendix E, including the sampling station name, location, land ownership, geologic setting, and a brief site description for each site. The sampled locations included four wells and eleven springs. Sample locations are shown in Figure 1.2-1.

Seven Springs is included as part of this investigation although it is separated from the Pajarito Plateau. This spring is located west of the recharge area for the Pajarito Plateau, but its major ion chemistry is similar to well LAOI(A)-1.1. Seven Springs and LAOI(A)-1.1 discharge and are completed, respectively, within the Otowi Member of the Bandelier Tuff and the Guaje Pumice Bed. Seven Springs discharges from the west side of Calaveras Canyon, about 400 m upstream of State Highway 126 and west of the Valles Caldera on the Jemez Plateau. There are several springs in the immediate vicinity; some discharge from alluvium and others from outcrops of densely welded rhyolite tuff. Samples were taken from the largest spring.

# **3.3.1 Springs within the Recharge Zone**

Springs in the recharge area west of and upgradient of the Laboratory include Apache Spring, upper Cañon de Valle Spring, Pine Spring, and the Water Canyon Gallery. Apache Spring issues in the

southern Sierra del los Valles (Figure 1.2-1). The spring discharges from colluvium consisting of blocks of the Tshirege Member of the Bandelier Tuff and Tschicoma Formation dacite in a matrix of volcanic sand and soil.

Upper Cañon de Valle Spring issues about 2.4 km west of State Highway 501. The spring is situated about 20 m above the bottom of upper Cañon de Valle in the Tshirege Member of the Bandelier Tuff. At this location, it appears that the Tshirege Member fills preexisting topography in the vicinity of the spring because downstream are major outcrops of preexisting Tschicoma Formation dacite.

Water Canyon Gallery is an improved spring occurring in the north branch of uppermost Water Canyon, about 1.3 km west of State Highway 501 and just west of the Pajarito Plateau. The spring issues from a tunnel that extends into a cliff of densely welded ignimbrite of the Tshirege Member of the Bandelier Tuff.

Pine Spring is located in upper Garcia Canyon about 6 km north of Los Alamos. Pine Spring discharges within the alluvium on the downthrown side of a north-south-trending fault juxtaposing boulder-bearing sediments of the Puye Formation (to the west) against mafic-to-intermediate composition lavas and overlying Puye deposits (to the east) (Smith et al. 1970, 09752; Kempter and Kelley 2002, 88777).

### **3.3.2 Sampling Stations on the Pajarito Plateau**

Wells LAOI(a)-1.1 (intermediate-perched system), LAO-B (the only well completed in the alluvium), Otowi-4 (regional aquifer), and Guaje-5 (regional aquifer) are positioned along the regional flow path downgradient from the recharge zone for the Pajarito Plateau (Figure 1.2-1).

Well LAOI(a)-1.1 is an observation well that was drilled in upper Los Alamos Canyon in 1994. It is screened within a perched zone in the Guaje Pumice Bed at the base of the Otowi Member of the Bandelier Tuff. Perched intermediate groundwater at the well occurs at a depth of 94.5 m.

Well LAO-B is an observation well drilled into valley-fill alluvium in upper Los Alamos Canyon west of the Laboratory boundary. The groundwater occurs within alluvium.

Guaje Canyon Well G-5 was completed in May 1951 to a depth of 608.8 m (Purtymun 1995, 45344) and was reliably used as a water supply well until it was plugged and abandoned in 1998. The initial static water level was 125 m below surface but through time the water level has descended as a result of production and drawdown (148 m in 1991). The production rate was about 1960 L/min. The screened interval and production horizon of the well were entirely within the Santa Fe Group.

Otowi-4 is a water supply well in Los Alamos Canyon that was completed to a final depth of 788.1 m in March 1990 (Stoker et al. 1992, 12017). Aside from a section of Miocene basalts, the screened interval at Otowi-4 is entirely within older fanglomerates from 340-m to 785-m depth.

## **3.3.3 Sampling Stations within the Discharge Zone**

Six springs are located within the discharge zone for the regional system. These include Spring 9B, Doe Spring, Spring 1, Pajarito Spring, Sacred Spring, and La Mesita Spring (Figure 1.2-1).

Spring 9B issues from the bottom of a basaltic lava flow on the northwest side of White Rock Canyon, roughly 200 m downstream of the mouth of Chaquehui Canyon. It is located in hydromagmatic deposits and flows of the Cerros del Rio volcanic field. The spring is about 25 m above the Rio Grande. Doe Spring is located in these same hydromagmatic deposits. It flows from lower Chaquehui Canyon, about 30 m above the canyon floor. Both springs discharge from the regional aquifer.

Spring 1 issues from a small bench about 40 m above the northeast side of the Rio Grande and about 1.5 km downstream of the Otowi Bridge. The bench occurs within a landslide complex made up of a variety of sediment types within the Santa Fe Group.

Pajarito Spring (Spring 4A of Purtymun 1995, 45344) issues from near the base of a landslide block in White Rock Canyon about 0.4 km west of the Rio Grande. This spring discharges from the regional aquifer. There are actually several discharge points for the spring, which collect to form a small creek. Rocks in the discharge channel of the spring consist primarily of Cerros del Rio basalt and minor rounded cobbles of quartzite, chert, and other lithologies. Parts of the matrix and fragments resemble lithologies in the Santa Fe Group.

Sacred Spring is a pool about 10 m in diameter located about 0.5 km north of the junction of State Highways 4 and 30 and about 100 m east of State Highway 30. Sacred Spring issues from unconsolidated sedimentary rocks of the Santa Fe Group.

La Mesita Spring is an outlier and is located in the discharge zone for the regional aquifer east of the Rio Grande. La Mesita Spring has been included in this investigation for geochemical comparison purposes. Statistical analyses from this spring, however, are not included with the other regional aquifer sampling stations because of its location and unique natural water chemistry. Groundwater representative of La Mesita Spring and wells at San Ildefonso Pueblo are characterized by higher concentrations of solutes, most notably of sodium, calcium, bicarbonate, and uranium, compared to supply wells on the Pajarito Plateau. La Mesita Spring issues on the northwest side of Buckman Mesa (La Mesita) about 500 m downstream of the Rio Grande Otowi Bridge. The uppermost source of water is about 20 m above river level. All rocks in this area consist of coalesced landslides (Dethier 1997, 49843). Older rocks within the landslides consist of unconsolidated sedimentary deposits of the Santa Fe Group. Along ridge crests, these older sediments are covered with coarse-grained gravels of the ancestral Rio Grande. Draperies of these gravels and basalt blocks derived from the Cerros del Rio volcanic field cover these slopes.

## **4.0 RESULTS**

## **4.1 Sample Collection, Preparation, and Evaluation**

The objective of this section is to describe methods of data validation conducted on groundwater samples collected during this investigation. Data validation considered holding times, experimental bias, and accuracy and precision of data.

The collection process consisted of taking filtered and nonfiltered groundwater samples at each of the 15 stations in up to 6 sampling rounds. One duplicate sample (filtered) was also collected per five groundwater samples for each sampling event. Groundwater samples analyzed for major cations, trace elements, metals, and radionuclides were either filtered through a 0.45-µm membrane or not filtered before sample preservation with concentrated nitric acid. Anion analyses, including sulfate, chloride, bromide, and fluoride, were performed on nonpreserved filtered and nonfiltered groundwater samples. Filtered samples were analyzed for DOC and DOC fractionation.

Chemical and radiochemical analyses performed by external contract laboratories (Paragon Analytics, Inc., Huffman Laboratories, and the University of Miami) are listed in Table 4.1-1. Paragon Analytics, Inc. also performed analyses for bicarbonate and anions using EPA methods (EPA 1987, 31732). In addition, Paragon Analytics, Inc. sent samples to a subcontractor laboratory, Huffman Laboratories, for DOC, DOC fractionation (humic acids), and dissolved silica analyses. These analyses were carried out using methods specific to the type of analysis (see Section 3.2.2). The external laboratory followed the

Environmental Restoration (ER) Project statement of work (SOW) (LANL 1995, 49738) for quality control (QC) of sample analyses for holding time and sample preservation, storage, and preparation.

Additional chemical analyses were provided by EES-6. Table 4.1-2 provides information on analytes, analytical instruments, EPA method numbers, and instrument detection limits (IDLs).

Analytical results of inorganic analytes were evaluated using the Laboratory QC data reported for laboratory blanks, laboratory duplicates, laboratory spike samples, laboratory control samples (LCSs), and calibration samples.

The data-validation process consisted of conducting a systematic baseline review followed by a more focused validation. Analytical results for trace metals and uranium (analyzed by LIKPA) were evaluated by following procedures identified in the ER Project baseline data validation standard operating procedure. This procedure applies a subset of the National Functional Guidelines for data review (EPA 1994, 48639; EPA 1994, 48640). The EPA National Functional Guidelines were also used to define the review conducted for the focused validation described in this section. The baseline validation used only the data reported by the laboratory on the forms provided as part of the deliverable, but the focused validation used the much more detailed information of the raw data provided by the laboratory. The focused validation included checks for sample-specific QC results, but the baseline validation applied QC results on a more global basis. The National Functional Guidelines (EPA 1994, 48639; EPA 1994, 48640) were applied as closely as possible to the anion, bicarbonate, dissolved silica, and total uranium analyses although these methods are not specifically covered by the guidelines.

## **4.1.1 Results of Data Validation**

The results for all analyses were accepted as qualified except for several metals and anions associated with water samples collected in February 1998 and reported by Paragon Analytics, Inc. Analytical results for specific metals were rejected because of interferences indicated in the preparation blank analyses, (discussed further in this section). The results for several anions were rejected because the samples were analyzed after the 48-hr holding time for nitrate, nitrite, and orthophosphate. The holding time problems are discussed further in Section 4.1.2.

# **4.1.1.1 Trace Element Analyses**

Groundwater samples were all prepared and analyzed following the EPA Contract Laboratory Program (CLP) SOW ILM 03.0 (EPA 1994, 48640). Technical holding times were met for all trace metal analyses. Analytes and IDLs for the trace elements and metals provided by Paragon Analytics, Inc. are given in Table 4.1-3.

The bias of the trace-element measurements was evaluated by the concurrent analysis of preparation and calibration blanks. There were several analytes detected above the IDL in several of the blanks reported by Paragon Analytics, Inc. in February 1998. Following the criteria given in the National Functional Guidelines for data review (EPA 1994, 48639), the results for these analytes were qualified as nondetected ("U") because the reported sample results were less than five times the greatest amount found in an associated blank. In addition, several analytes were detected at a negative amount in the preparation blanks analyzed. Selected trace elements were detected in the blanks at levels that were negative (relative to the initial calibration) and greater in absolute value than the amounts detected in samples in the same batch. Following the criteria given in the National Functional Guidelines for Data Review (EPA 1994, 48639), the results for these analytes were qualified in one of two ways:

- The results were rejected (qualified with an "R") when the reported sample results were less than the estimated detection limit or less than the absolute value of the amount found in the blank, or
- The results were qualified as estimated with a potential low bias (qualified with a "J") when the reported sample results were greater than the absolute value of the amount found in the preparation blank, but less than five times the absolute value of the amount found in the preparation blank.

Rejected analytical results occurred for 36 groundwater samples, consisting of 47 analyses of aluminum (7 analyses), beryllium (1 analysis), copper (7 analyses), lead (1 analysis), manganese (8 analyses), mercury (21 analyses), and zinc (2 analyses), collected during February, April, July, September, and October 1998 (Paragon Analytics, Inc.).

The bias of the trace-element measurements was also assessed by analysis of matrix spike samples. All spike recoveries were acceptable with no apparent bias for all trace-metal analytes that were spiked into the water matrices.

The accuracy of the trace-element measurements was checked by the concurrent analysis of aqueous LCSs. Results for individual samples were qualified on the basis of the LCS analyzed in the same batch according to the criteria given in the National Functional Guidelines (EPA 1994, 48639). No data qualifiers were added to the sample results on the basis of the LCS recoveries.

The precision of the inorganic measurements was assessed by the analysis of laboratory duplicate samples. The results for one laboratory duplicate sample were reported for each batch in the data set. The relative percent differences (RPDs) for duplicate measurements of the target analytes were acceptable, and no results were qualified with deficiencies of laboratory-induced errors based on the duplicate sample analyses. The analytical data are useable as qualified by this process.

# **4.1.1.2 Anion and Bicarbonate Analyses**

Groundwater samples were prepared and analyzed following EPA Method 310.0 for bicarbonate using titration and EPA Method 300.0 for anions using ion chromatography. Technical holding times were met for all analyses except nitrite, nitrate, and orthophosphate collected during February 1998, which were analyzed by Paragon Analytics, Inc. outside the 48-hr holding time. The results for these analytes were rejected for use (qualified "R") because of the missed holding times and because the concentrations of nitrite, nitrate, and orthophosphate are affected by the length of holding times. Sample duplicates were collected and analyzed within appropriate holding times by EES-6 in February 1998, and these results were used for data analysis and interpretation.

The bias of the anion measurements was evaluated by the concurrent analysis of blanks. Interference for orthophosphate was detected above the MDL in some of the blanks associated with several water samples collected in February 1998. The laboratory raised the detection limit for the affected samples to 0.2 mg/L so the interference would not be detected in the blank. The results were not qualified for blank contamination because orthophosphate was then not detected in the affected samples.

The accuracy of the anion and bicarbonate measurements was monitored by the concurrent analysis of aqueous LCSs. Results for individual samples were evaluated on the basis of the LCS analyzed in the same batch, according to the criteria given in the National Functional Guidelines (EPA 1994, 48639). No data qualifiers were added to the sample results on the basis of the LCS recoveries.

The precision of the anion and bicarbonate measurements was assessed by the analysis of laboratory duplicate samples. The results for one laboratory duplicate sample were reported for each batch in the data set. The RPDs for duplicate measurements of the target analytes were acceptable, and no results were qualified based on the duplicate sample analyses. The analytical data are useable as qualified by this process unless the results were rejected as described above.

### **4.1.1.3 Dissolved Silica Analyses**

Groundwater samples were prepared and analyzed following the EPA Method 370.1 for silica analyses. The analyses were conducted using colorimetry. Technical holding times were met for all analyses. The bias of the dissolved silica measurements was monitored by the concurrent analysis of blanks. No problems were noted with the blanks.

The accuracy of the dissolved silica measurements was assessed by the concurrent analysis of aqueous LCSs. Results for individual samples were qualified on the basis of the LCS that was analyzed in the same batch, according to the criteria given in the National Functional Guidelines (EPA 1994, 48639). No data qualifiers were added to the sample results on the basis of the LCS recoveries.

The precision of the dissolved silica measurements was assessed by the analysis of laboratory duplicate samples. The results for one laboratory duplicate sample were reported for each batch in the data set. The RPDs for duplicate measurements of the target analytes were acceptable, and no results were qualified based on the duplicate sample analyses. The analytical data are useable as qualified by this process.

#### **4.1.1.4 Uranium Analyses**

Groundwater samples were prepared and analyzed for uranium following an external laboratory procedure (Paragon Analytics, Inc.). The analyses were conducted using LIKPA methods. Technical holding times were met for all analyses. The bias of the total uranium concentration measurements was monitored by the concurrent analysis of blanks. No problems were noted with the blanks.

The accuracy of the total uranium measurements was assessed by the concurrent analysis of aqueous LCSs. Results for individual samples were evaluated on the basis of the LCS that was analyzed in the same batch, according to the criteria given in the National Functional Guidelines for data review (EPA 1994, 48639). No data qualifiers were added to the sample results on the basis of the LCS recoveries.

The precision of the total uranium measurements was assessed by the analysis of laboratory duplicate samples. The results for one laboratory duplicate sample were reported for each batch in the data set. The RPDs for duplicate measurements of the target analytes were acceptable, and no data qualifiers were added to the results, based on the duplicate sample analyses. The analytical data are useable as qualified by this process.

#### **4.2 Statistical Analyses of 1997 to 2000 Groundwater Data**

This section provides results of statistical analyses of a comprehensive database of organic and inorganic chemical, stable isotope, and radionuclide analyses of 566 groundwater analyses from 196 samples collected from 15 springs and wells located in and around the Laboratory. The region considered in this investigation extends from the western edge of the Jemez Mountains eastward to the Rio Grande and from Frijoles Canyon northward to Garcia Canyon. Figure 1.2-1 shows the fifteen stations sampled for this investigation. The sampling stations, associated aquifer types, and coordinated formations are summarized in Table 4.2-1. La Mesita Spring and Pajarito Spring were not included with the other

sampling stations for statistical analyses because La Mesita Spring represents a different hydrologic system (Rio Grande Valley) with its unique water chemistry, and Pajarito Spring (Spring 4A) contains nitrate (as nitrogen) (1 mg/L) and perchlorate (0.5 µg/L) concentrations that are greater than the other background sampling stations.

### **4.2.1 Statistical Methods and Results**

### **4.2.1.1 Statistical Methods**

Several data-preparation steps were needed before statistical analyses could be performed on the water chemistry data. First, the data were subjected to a systematic data validation (see Section 4.1.1). Second, the data were inspected for suspect values that were exceptionally high or low relative to the rest of the data. All analytical data, excluding low-level tritium and DOC fractionation, were the subject of focused data validation (also reported in Section 4.1.1). Third, the data qualifiers were reviewed, and any data identified as R-qualified were not used in statistical analyses. Fourth, nondetected sample results were noted. Nondetected sample results were typically reported as less than (<) the IDL for that chemical. Values reported as nondetected by the analytical laboratory were replaced by both the detection limit and one-half of the detection-limit value for statistical analyses. This replacement method is recommended by the EPA when the frequency of nondetected values is relatively low (EPA 1992, 54947).

Analytical suites, field parameters, and sampling dates for the background stations are provided in Appendix A. Sample results and data qualifiers based on systematic and focused validation for inorganic analytes and radionuclides are provided in Appendix B. Sample results and data qualifiers for other analytes (water-quality parameters and stable isotopes) are also provided in Appendix B.

The data were reviewed to identify laboratory-reporting or analysis errors. During this review process, two uranium results for samples collected on December 16, 1999, were found to be inconsistent between methods and with other uranium results for the locations sampled. Uranium results (using ICPMS) for sample numbers CABG-99-0006 (La Mesita Spring) and CABG-99-0007 (Sacred Spring) appeared to have been switched. Table B-1.2 has been corrected to place the samples under the correct spring location, as indicated above.

The statistical analysis of the background data involves several exploratory data analysis (EDA) tools, including normal quantile plots of untransformed data, box plots to compare possible data groups, linear regression analysis and scatterplots, and statistical data summaries. The purpose of EDA is to identify possible outliers in these data, understand relationships between analytes, evaluate parametric and nonparametric statistical modeling options, and determine the frequency of nondetect values by analyte and by potential data subpopulations. Four types of data plots were made, as explained below.

*Normal quantile plots*: A normal quantile plot is a particular type of quantile plot in which the data set concentrations are plotted in increasing order and spread out in a manner that allows comparison of their distribution to that of a theoretical distribution: the standard normal distribution. The quantiles of the data set (*y*-axis) are plotted against the quantiles for a standard normal (*x*-axis). The quantiles of a standard normal (i.e., a normal with a mean = 0 and a standard deviation = 1) are those for the theoretical distribution and can be found in published tables of the cumulative normal distribution. For example, the 50th quantile is 0, the 90th quantile is approximately 1.282, the 95th quantile is about 1.645, etc. If the data are derived from a normal statistical distribution, the points in the plot will lie close to the diagonal straight line overlying the data points. The subsets of the data set that differ the most from those expected from a normal distribution are seen as points straying from the line.

*Box plots*: Box plots are used to show differences between two or more sample locations or other data groupings. Box plots summarize information about the shape and spread of the distribution of concentrations for an analyte. Box plots consist of a box and a (median) line across the box. The *y*-axis displays the observed concentrations in the reported units. The area enclosed by the box shows the concentration range containing the middle half of the data; that is, the lower box edge is at the 25th percentile and the upper box edge is at the 75th percentile. The height of the box is a measure of the spread of the concentrations. The horizontal line across the box represents the median (50th percentile) of the data, a measure of the center of the concentration distribution. If the median line divides the box into two approximately equal parts, the shape of the distribution of concentrations is symmetric; if not, the distribution is skewed or nonsymmetrical. All concentrations are plotted as points overlying the box plot.

*Regression analysis and scatter plots*: Regression analysis provides a measure of the association between pairs of variables. An *x-y* scatter plot is used to graphically depict this relationship. Linear regression analysis provides a measure of the degree of fit (coefficient of determination or  $r^2$ ) and the slope/intercept of the least-squares linear model. The coefficient of determination can potentially range between 0 and 1. A coefficient of determination of zero indicates no relationship between the two measurements, and a coefficient of determination of 1 indicates a linear relationship between the measurements.

*Scatter plot matrix*: The scatter plot matrix is used to illustrate the relationship between more than two measurements. The scatter plot matrix shows the paired sample results, and the ellipse shown on each scatter plot encloses 95% of the data. Cases where the ellipse approaches a line indicate a highly significant statistical correlation between measurements.

### **4.2.1.2 Statistical Results**

Results of statistical analyses, including minimum, mean, median, maximum, one sigma (standard deviation) error, and percent coefficient of variation, number of samples, number of rejected samples, and number of nondetected values for alluvial groundwater, volcanic perched groundwater, and the regional aquifer are provided in Tables 4.2-2a through 4.2-2g; 4.2-3a through 4.2-3g; 4.2-4a through 4.2-4g; 4.2-5a through 4.2-5g; and 4.2-6a through 4.2-6g. Table 4.2-2b provides results of statistical analyses for alluvial groundwater (well LAO-B and Pine Spring), Tables 4.2-3a through 4.2-3g provide results for perched-intermediate groundwater (Apache Spring, Seven Springs, Water Canyon Gallery, upper Cañon de Valle, and well LAOI(A)-1.1), and Tables 4.2-4a through 4.2-4g provide results for the regional aquifer (wells Otowi-4 and Guaje-5 and Doe Spring, Spring 9B, Sacred Spring, and Spring 1). Pajarito Spring (Tables 4.2-6a through 4.2-6g) and La Mesita Spring (Tables 4.2-5a though 4.2-5g) are analyzed and summarized separately.

Statistical results for both filtered and nonfiltered samples are provided in Tables 4.2-2a through 4.2-2g, 4.2-3a through 4.2-3g, 4.2-4a through 4.2-4g, 4.2-5a through 4.2-5g, and 4.2-6a through 4.2-6g. They include pre- and post-1997 analytical results (combined and separate) using 0.5 and 1.0 detection limits. Several analytes, including antimony, beryllium, cadmium, lead, thallium, and uranium, had high IDLs, which increase the mean, median, maximum, standard deviation, and coefficient of variation for the pre-1997 data. For these reasons, the post-1997 data are also included separately because the IDLs for several analytes are lower using more advanced instrumentation. During the period from 1997 to 2000, the background locations were sampled during six sampling events to provide equal information over time at each location. The intended goal was to characterize background concentrations; therefore, analytical methods with low IDLs were specified. Figures B-1 through B-17 in Appendix B of this report present the concentration results over time for all analytes. The plots illustrate the improvement of detection limits for analytes with large pre-1997 IDLs and show the relative consistency attained, beginning in 1997. The

post-1997 analytical results are more representative of background concentrations within the three aquifer types. Table 4.2-2e (Alluvial GW), Table 4.2-2e (alluvial groundwater), Table 4.2-3e (perchedintermediate volcanic rock), and Table 4.2-4e (regional aquifer) are recommended for evaluating the statistical properties of background concentrations of solutes within the three aquifer types. They also provide a more conservative approach for establishing background concentrations in groundwater.

Analytical results for major ions and trace elements reported by EES-6 and Paragon Analytics, Inc. have been combined for each analyte. This data summary includes the field duplicate samples collected during the investigation and the three samples collected by NMED. Tables 4.2-2a through 4.2-2g; 4.2-3a through 4.2-3g; 4.2-4a through 4.2-4g; 4.2-5a through 4.2-5g; and 4.2-6a through 4.2-6g list summaries for 111 analytes. The detection frequency for water chemistry analytes varies greatly from 0% to 100%. The background concentrations of antimony and cadmium with <20% detection rate were evaluated by considering minimum values, including the detection limit and half the detection limit. Beryllium, cadmium, cobalt, lead, selenium, silver, and thallium were typically not detected in the background water samples.

# **4.2.1.2.1 Evaluation of Field Duplicate Samples**

As a quality assessment measure for the investigation, field duplicate samples were collected and submitted for analysis to contract analytical laboratories or the EES-6 analytical laboratory. Field duplicate samples provide a measure of the variability within a sampling event (sample collection and preparation) and analytical laboratory measurement variability.

The differences between field duplicate measurements for all water-chemistry analytes were assessed by comparing concentrations for samples noted as "duplicate" and "sample" in Appendix B. Fifteen analytes were selected as representatives of the more frequently detected analytes. A comparison of field duplicates to the original sample for these analytes is provided in Figure 4.2-1.

The scatter plots in Figure 4.2-1 illustrate that field duplicate sample results are identical, or nearly identical, to the original sample result for most of these analytes. The field duplicate sample results were also unbiased, as shown by the linear regression slope being close to or equal to 1.0 and the intercept being close to 0.0. The coefficient of determination ( $r^2$ ) also illustrates the strong agreement of field duplicate results to original sample results.

Ammonium provides an example of the variability observed for less frequently detected analytes. Although a strong relationship occurs between the field duplicate results and the original sample results, more variation is evident on the ammonium scatter plot (Figure 4.2-1). Infrequently detected analytes tend to have more sample results near the IDL, which is a concentration range associated with greater variability in the laboratory measurement process. Thus, reported values for infrequently detected analytes need to be evaluated more carefully for use as background (no Laboratory impact) concentrations.

# **4.2.1.2.2 Comparison of Results by Analytical Laboratory and Method**

For this investigation, sample results from the contract analytical laboratories were compared to the EES-6 analytical laboratory as another quality-assurance (QA) measure. The laboratories used different analytical methods for some analytes (e.g., uranium, tritium, and trace metals).

Contract and EES-6 analytical laboratory sample results for seven inorganic chemicals and six waterquality parameters (anions, cations, silica, and TDS) were compared. These analytes were selected based on the number of samples submitted to each laboratory and the detection frequency. Selection preference was given to analytes detected by both EES-6 and the contract laboratory so that measured values were compared rather than IDLs.

Charge balance errors calculated from groundwater samples analyzed at the EES analytical laboratory range from -3% to +61%. About 87% of the charge balance errors are within the EPA-recommended value of ±10%. The anomalous charge balance error of +61% occurs for a filtered water sample collected from the upper Cañon de Valle Spring.

Reporting limits and analytical methods provided by EES and Paragon Analytics, Inc. are shown in Table 4.2-7. The EES-6 laboratory generally provides additional analytes with lower reporting limits using atomic absorption (AA) methods (including GFAA and HAA) as compared to Paragon Analytics, Inc., using ICPAES. Paragon Analytics, Inc. generally reports concentrations of calcium, iron, and strontium above reporting limits, but concentrations of antimony, arsenic, beryllium, boron, cadmium, chromium, lead, mercury, molybdenum, selenium, silver, and tin are less than detection (U-qualified sample results are provided in Appendix B).

Concentrations of aluminum, barium, copper, manganese, nickel, thallium, titanium, vanadium, and zinc are generally detected, but sometimes they are below the limits of quantification or reporting limits (J-qualified sample results). Concentrations of chloride, sulfate, bicarbonate, calcium, magnesium, sodium, and potassium reported by EES-6 and Paragon Analytics, Inc. are in good agreement and are also within experimental error. The reporting limits are sample specific, depending on matrix interferences and the general nature of the groundwater sample.

The results of this comparison indicate that the analytical results from the EES-6 analytical laboratory are comparable to the values reported by the contract analytical laboratories (Figure 4.2-2). Results for barium, calcium, magnesium, potassium, and chloride are nearly identical between the EES-6 and contract analytical laboratories, as illustrated by the scatter plots for these analytes (Figure 4.2-2). The linear regression statistics for barium, calcium, potassium, magnesium, chloride, and nitrate are close to the ideal slope of 1.0, intercept of 0.0, and coefficient of determination of 1.0. Greater variability is seen for the between-laboratory comparisons (EES-6 and Paragon Analytics, Inc.) for selected analytes (e.g., barium, tritium, manganese, and TDS, as shown in Figures 4.2-1 and 4.2-2).

For other analytes, the sample results from the EES-6 analytical laboratory correlate to the contract analytical laboratory, but positive or negative bias between the laboratories can be found. The EES-6 analytical laboratory sample results for manganese, sodium, bicarbonate, and TDS are greater than the comparable contract analytical laboratory sample results (the slope is greater than 1.0 for these analytes; see Figure 4.2-2). The EES-6 analytical laboratory sample results for silica and fluoride are less than the comparable contract analytical laboratory sample results (the slope is less than 1.0 for these analytes; see Figure 4.2-2).

Two methods, ICPMS and LIKPA, were used to determine uranium concentrations in groundwater. These methods were used for 27 samples. The concentrations reported for ICPMS and LIKPA agree reasonably well, as noted in Section 4.2.1.1.

Tritium was determined at two contract laboratories: Teledyne and the University of Miami. The University of Miami's method is designed for low-level tritium detection, while Teledyne uses the more standard method that has a nominal IDL of 300 pCi/L. The results from these analytical methods correlate weakly (Figure 4.2-2). The University of Miami data are preferred for resolving differences in low levels of tritium.

Trace metals were analyzed by ICPMS in the last sampling round in 2000 to supplement previous inorganic chemical ICPAES results. The ICPMS method was needed to obtain IDLs at concentrations less than the EPA MCLs for antimony, beryllium, cadmium, lead, thallium, and uranium. Antimony was detected above the IDL of 0.1 µg/L in <3% of the samples.

### **4.2.1.2.3 Spatial Trends in Water Chemistry Results**

Spatial trends for average dissolved concentrations of selected analytes are shown in Figure 2.2-1, which illustrates the spatial distribution of the background sampling stations for the three identified aquifer types: alluvium, perched-intermediate, and the regional aquifer. Five of the eight regional aquifer stations are located in a cluster northeast of the Laboratory boundary. The perched-intermediate stations are in the Jemez Mountains and Sierra de los Valles. There are two alluvial background sampling stations located northwest and west of the Laboratory.

The average tritium concentrations for sampling stations located near recharge areas (Water Canyon Gallery, Apache Spring, Upper Cañon de Valle, and Pine Spring) in the Sierra de los Valles are greater than from springs that discharge to the Rio Grande. In general, concentrations of other analytes (specific conductance and major cations and anions) follow an opposite pattern, where higher concentrations (increasing residence times) are reported for locations with low tritium (smaller amounts of recent recharge). Some sample locations are spaced closely together, and the pair of locations most closely spaced and also emerging from the same aquifer type (Doe Spring and Spring 9B) tend to have similar average concentrations for the analytes illustrated in Figure 4.2-3. Concentrations of dissolved uranium range from 0.1 to 0.8 µg/L in the Sierra de los Valles and beneath the Pajarito Plateau. Higher concentrations of natural dissolved uranium occur along the Rio Grande northeast of the Laboratory boundary. La Mesita Spring has an average concentration of dissolved uranium of 9.0 µg/L. Average concentrations of dissolved barium generally increase from the Sierra de los Valles to Sacred Spring and La Mesita Spring.

## **4.2.1.2.4 Evaluation of Analytes**

The entire list of analytes from the contract analytical laboratories and the EES-6 analytical laboratory was trimmed to those that are most important, based on regulatory needs and conceptual geochemical and hydrogeologic framework understanding. Table 4.2-8 lists the analytes, the applicable regulatory agency (NMED, EPA, and DOE), the detection rates for the analytes, and the sources of the data (analytical laboratory). Statistical plots for these analytes are provided in Appendix C, and a brief narrative is provided below for each analyte. The statistical plots provide a visual summary of post-1997 data from the combined results from all laboratories.

*Field Measurements:* Temperature, turbidity, specific conductance (conductivity), and pH were measured for nearly all sampling events at each location. Temperature increases with depth in a geothermal gradient from the alluvial stations to the volcanic stations and is greatest in the regional sampling locations (Figure C-1). Specific conductance also varies with rock type (Figure C-2). The pH of these waters tends toward being slightly alkaline and is most variable for the volcanic rocks (Figure C-3).

*Aluminum:* This trace element was detected in about 62% of the samples. The aluminum sample results for Pine Spring were outliers and are roughly 10 to 100 times greater than sample results for other locations (Figure C-4). The sample results for most locations are variable. The aluminum data appear to be derived from a mixture distribution that suggests multiple populations. The volcanic rock aquifer appears to have locations with the highest and most variable aluminum concentrations.

*Antimony:* This trace element was detected in about 5% of the samples. The last round of sampling in late 1999 and early 2000 analyzed antimony by ICPMS and achieved IDLs (Figure C-5).

*Arsenic:* This trace element was detected in about 63% of the samples. No outliers are present, and most of the detected sample results appear to be from the regional aquifer (Figure C-6). Concentrations are typically consistent by sample location.

*Barium:* This trace element was detected in about 99% of the samples. No outliers and no significant differences occur by aquifer type (Figure C-7). Concentrations are typically consistent by sample location. Sample results are multimodal (perhaps bimodal), suggesting that two or more underlying statistical populations occur.

*Beryllium:* Statistical plots for beryllium are provided in Figure C-8. This trace element was detected in about 8% of the samples. Lower IDLs were obtained in the last two sampling rounds when this analyte was quantified by ICPMS.

*Boron:* This trace element was detected in about 77% of the samples. There are no outliers, and the regional aquifer has the greatest boron concentrations (Figure C-9).

*Cadmium:* Statistical plots for cadmium are provided in Figure C-10. This trace element was detected in about 3% of the samples.

*Calcium:* This major cation was detected in 100% of the samples. There are no outliers, and the regional aquifer has the greatest concentrations (Figure C-11). Sample results are generally consistent by location.

*Chromium:* This trace element was detected in about 48% of the samples. One outlier was noted: the result for sample RE16-98-9012 was 44.7  $\mu$ g/L, or about a factor of ten larger than other total chromium results. The nonfiltered paired result was 3.2 µg/L, suggesting this filtered sample result for total chromium is anomalous. Most locations exhibit low variability, and little difference in concentration occurs by aquifer type (Figure C-12).

*Cobalt:* Statistical plots for cobalt are provided in Figure C-13. This trace element was detected in about 8% of the samples.

*Copper:* Statistical plots for copper are provided in Figure C-14. This trace element was detected in about 49% of the samples.

*Iron:* This trace element was detected in about 55% of the samples. The iron sample results for Pine Spring were outliers and are roughly 10 to 100 times larger than sample results for other locations (Figure C-15). The sample results for most locations are variable. The iron data appear to be derived from a mixture distribution that suggests multiple statistical populations.

*Lead:* Statistical plots for lead are provided in Figure C-16. This trace element was detected in about 15% of the samples.

*Magnesium:* This major cation was detected in about 98% of the samples. Sample results for location Otowi-4 are outliers from the rest of the data (Figure C-17). Magnesium shows little variation by sample locations.

*Manganese:* This trace element was detected in about 57% of the samples. There are no outliers, and concentrations vary within a sampling location (Figure C-18). No significant differences between concentrations occur by aquifer type.

*Mercury:* Statistical plots for mercury are provided in Figure C-19. This trace element was detected in about 29% of the samples.

*Molybdenum:* Statistical plots for molybdenum are provided in Figure C-20. This trace element was detected in about 27% of the samples.

*Nickel:* This inorganic chemical was detected in about 18% of the samples (Figure C-21). One outlier was noted; the result for sample RE16-98-9012 was 19.8 µg/L or about two times larger than other nickel results. The nonfiltered paired result was  $0.9 \mu g/L$ , suggesting that this filtered sample result for nickel is anomalous. The nickel sample result for sample CABG-00-0057 may also be an outlier, but it has no paired nonfiltered result for comparison. Nickel concentrations from Pine Spring are greater than for other locations (except for the two outliers discussed above).

*Perchlorate:* See Section 4.2.1.2.5.

*Potassium:* This major cation was detected in 100% of the samples. No outliers and no notable differences occur between aquifer types (Figure C-22). Concentrations are generally consistent for a location.

*Selenium:* Statistical plots for selenium are provided in Figure C-23. This trace element was detected in about 11% of the samples.

*Silver:* Statistical plots for silver are provided in Figure C-24. This trace element was detected in about 5% of the samples.

*Sodium:* This major cation was detected in 100% of the samples. There is one outlier for Apache Spring (sample CABG-00-0047). Apache Spring water contains a component of road salt runoff, based on measured concentrations of sodium and chloride. The regional aquifer concentrations are greater than other aquifer types, and sodium concentrations are mostly consistent values for a sampling location, except for Apache Spring, as noted above (Figure C-25).

*Strontium:* Statistical plots for strontium are provided in Figure C-26. This trace element was detected in 99% of the samples.

*Thallium:* This trace element was detected in about 7% of the samples (Figure C-27).

*Uranium:* This trace element was detected in 100% of the contract laboratory samples; the EES-6 results were not used to characterize this analyte. Uranium concentrations are much greater in selected regional aquifer locations (La Mesita Spring and Spring 1), and the concentration distribution is multimodal because of the low variability within locations and large differences between some locations (Figure C-28).

*Zinc:* This trace element was detected in about 44% of the samples. Otowi-4 sample results are greater than other locations, and the concentrations differ more by location than by aquifer type (Figure C-29). Moderate variation occurs within sampling locations.

*Alkalinity:* This water-quality parameter was detected in 100% of the samples. Alkalinity is greater in regional aquifer locations (Figure C-30).

*Ammonium:* This trace cation was detected in about 73% of the samples. Ammonium concentrations were greatest at location LAOI(A)-1.1 and otherwise did not differ greatly between locations or location groups (Figure C-31).

*Bicarbonate:* This major anion was detected in 100% of the samples. Bicarbonate is greater in regional aquifer locations (Figure C-32).

*Dissolved organic carbon:* This water-quality parameter was detected in 100% of the samples. DOC was greatest for the volcanic rock aquifer locations (Figure C-33).

*Chloride:* This major anion was detected in 100% of samples. Apache Spring water contains a component of road salt runoff, based on measured concentrations of sodium and chloride. Chloride was greatest in the first two sample events for Apache Spring; otherwise, chloride did not vary significantly between location groups (Figure C-34).

*Fluoride:* This major anion was detected in 94% of the samples. Fluoride concentrations varied with aquifer type (Figure C-35).

*Nitrate:* This major anion was detected in about 87% of the samples. Concentrations of nitrate varied by location but did not vary significantly by aquifer type (Figure C-36).

*Nitrite:* Statistical plots for nitrite are provided in Figure C-37. This major anion was detected in about 14% of the samples.

*Silica:* This water-quality parameter was detected in 99% of the samples. Silica varies by location but does not vary significantly by aquifer type (Figure C-38).

*Total dissolved solids:* This water-quality parameter was detected in 100% of the samples. TDS increase from the alluvial location to volcanic rock locations and are greatest for the regional aquifer locations (Figure C-39). The overall TDS distribution is multimodal because of this variation between aquifer types.

*Stable isotopes:* The statistical plots for stable isotopes are provided in Figures C-40 to C-43. The deuterium and oxygen plots show that Seven Springs differs from other sample locations because of its elevation and location west of the Laboratory.

*Gross alpha radiation:* This radioactivity measure was detected in about 76% of the samples. La Mesita Spring has greater gross alpha activity than other locations, and no other differences between location groups are significant (Figure C-44). The higher gross alpha activity is the result of natural uranium and its decay products.

*Americium-241:* This radionuclide was detected in about 16% of the samples. Nearly all of the detected sample results for this radionuclide came from a single sampling event in 1997 (Figure C-45), which raises questions regarding possible analytical laboratory problems with these values.

*Plutonium-238:* Statistical plots for plutonium-238 are provided in Figure C-46. This radionuclide was detected in about 5% of the samples.

*Plutonium-239/240:* Statistical plots for plutonium-239/240 are provided in Figure C-47. This radionuclide was detected in about 5% of the samples.

*Isotopic uranium:* The statistical plots for isotopic uranium are provided as Figures C-48 to C-50. These plots exhibit similar trends to those already discussed for uranium. Uranium sample results show disequilibrium between isotope ratios compared to natural uranium isotope ratios in solid media. This phenomenon has been noted in water samples collected in other parts of the world, and the ratios of natural uranium (and uranium daughters) have been shown to vary based on the temperature and mineral content of groundwater (Hakam et al. 2000, 70168).

*Strontium-90:* This radionuclide was not detected in the samples. Thus, the statistical plots (Figure C-51) present only instrument noise and not strontium-90 concentrations.

*Tritium:* This radionuclide was characterized using University of Miami results. It was detected in 100% of the samples. Tritium varies by location and exhibits a decreasing trend from the alluvial location to the volcanic rock location and to the regional aquifer locations (Figure C-52).

In summary, major cations (calcium, magnesium, sodium, and potassium), major anions (bicarbonate, chloride, and sulfate) and silica were measured in all background water samples. Fluoride was also measured in all of the samples, but nitrate, nitrite, and uranium had variable detections for the post-1997 analytical results. Other trace elements showed considerable ranges in which beryllium, cadmium, cobalt, copper, iron, lead, mercury, molybdenum, selenium, silver, and thallium were detected is less than 30% of the post-1997 sampling rounds.

The IDLs for antimony, arsenic, barium, beryllium cadmium, chromium, copper, lead, mercury, nickel, and selenium using ICPAES were below the respective IDLs promulgated by the EPA. The MDLs using ICPAES for other constituents, including aluminum, chloride, fluoride, iron, manganese, silver, sulfate, and zinc, are below their respective secondary levels. Radionuclides derived from fallout, including americium-241, plutonium-238, 239/240, and cesium-137, were generally not detected, except during one sampling round conducted in August 1997. Tritium was more frequently detected in groundwater samples collected from springs within the Sierra de los Valles, alluvial well LAO-B, Seven Springs, and perchedintermediate well LAOI(A)-1.1. Strontium-90 was not detected in the background water samples. On the whole, analytical results for background inorganic species and radionuclides are of high quality and may be applied to Laboratory sites.

Data for the other analytes (major ions, stable isotopes, DOC fractionation, and a majority of trace elements) are acceptable within their detectable ranges.

# **4.2.1.2.5 Low-Level Perchlorate**

The ubiquitous nature of trace levels of perchlorate (<1 µg/L) in groundwater near the Laboratory and northern New Mexico was determined by both the NMED and the Laboratory (NMED 2004, 88768). Widespread and consistent low-level detection of the chemical in nonhuman-impacted groundwater samples collected from local springs and wells are the basis for this interpretation. The concentration and persistence of perchlorate in both spatial and temporal dimensions, however, are not yet fully understood. The NMED and the Laboratory undertook a preliminary investigation to determine the concentration of perchlorate in selected waters within the northern Rio Grande Basin.

Sampling sites for low-level perchlorate included Sandia Spring, Spring 1, Spring 2, Springs 5, 5A, 5B, Springs 6, 6A, Spring 8A, and Springs 9, 9A, 9B, 9C for the regional aquifer. Perched intermediate volcanic sites included Alamo Canyon 10.3 Spring, Barbara's Spring, Campsite Spring, CdV-5.0 Spring, PC Spring, Colonel Spring, Water Canyon Gallery, Yak Spring, Young Spring, Pajarito Ski Well #2, and well LAOI(A)-1.1.

NMED compiled 76 low-level perchlorate results from 47 groundwater wells and springs within the northern Rio Grande Basin, with 56 of these samples collected around the Pajarito Plateau (NMED 2004, 88768). All water samples were selected based on technical considerations such as aquifer location, age, and water quality. Six different groundwater zones were sampled, with about half representing the regional aquifer beneath the Laboratory.

The NMED-selected sample stations were verified as background candidates through the analysis of major ions, including chloride and nitrate. These supplemental water-quality parameters showed sample results indicative of natural levels of nitrate (as N) at less than 0.5 mg/L. Additionally, tritium was measured because it can be found as a naturally occurring radioactive isotope of hydrogen that is commonly used for groundwater dating and to provide estimates on residence times and flow paths. Tritium results, coupled with local hydrogeologic relationships, show that springs located on the eastfacing slope of Sierra de Los Valles represent young water (<60 yr) in the early stage of the local hydrologic cycle. Most springs within White Rock Canyon illustrate old water (>60 yr) discharging at the end of the hydrologic cycle.

The NMED and Laboratory study exclusively used a more sensitive liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS) method (EPA SW846 8321MA) that is able to detect perchlorate at 0.05 µg/L or ppb. The conventional EPA method (SW846 314.0) is less sensitive and can only detect perchlorate at 4 ppb.

The 56 analytical results for groundwater show an average Laboratory background perchlorate concentration of 0.27  $\pm$  0.08 (1  $\sigma$ ) ppb or  $\mu$ g/L (Table 4.2-9). The minimum and maximum concentrations of perchlorate were 0.05 and 0.46 µg/L, respectively (Table 4.2-9). Only one water sample collected near the Pajarito Plateau had a perchlorate concentration of less than  $0.05 \mu g/L$  (Table 4.2-9), the IDL for LC-MS/MS.

Seven precipitation samples were collected and analyzed using the LC-MS/MS method to rule out the presence of trace levels in precipitation as a source for the perchlorate in groundwater. Perchlorate was not detected in these samples above the IDL of 0.05 µg/L. In late August 2004, two additional rain samples were collected and analyzed by NMED using a method similar to LC-MS/MS but with an IDL of 0.0012 µg/L or about 40 times lower than that of the LC-MS/MS method. Although preliminary and not yet validated, the results show that perchlorate may be present in these precipitation samples at 0.006 and 0.017 µg/L.

## **4.3 Summary of Interlaboratory Comparison of Stable Isotopes, Tritium, and Uranium**

This section presents summaries of interlaboratory comparisons of analytical data for stable isotopes of hydrogen and oxygen, tritium, and uranium. The analyses for stable isotopes are performed for nonregulatory purposes, including determining the origin, recharge elevation, and relative age of the groundwater sample; however, uranium is measured for both regulatory and hydrogeochemical purposes. For this investigation, four separate university laboratories, one commercial laboratory, and a government laboratory performed stable isotope analyses. One university analytical laboratory and a commercial laboratory provided analytical results for tritium. Two commercial laboratories performed uranium analyses using LIKPA and ICPMS. Analytical results varied with each laboratory, depending on the precision, accuracy, and method of analysis.

## **4.3.1 Analytical Comparisons, Stable Isotopes**

At the beginning of this investigation, EES-6 personnel used the UWM to provide analyses of stable isotopes (hydrogen and oxygen,  $\delta$ D, and  $\delta^{18}$ O) for background waters sampled as part of this investigation. Within a year, EES-6 personnel noticed that UWM's analytical results were shifted to slightly higher (heavier) isotope values compared to data received in the past from sites previously sampled. Figure 4.3-1 compares  $\delta$ D vs  $\delta^{18}$ O "same-site" data reported by UWM and by previous laboratories. The UWM data from 1997 are systematically displaced roughly +5‰ in  $\delta$ D and about -0.5‰ to -1.5‰ in  $\delta^{18}$ O compared to previous stable isotope data collected between 1978 to 1993.

Coincidentally, EES-6 personnel used UWM during 1996 and 1997 for stable isotope analyses of geothermal fluids for a project in Dixie Valley, Nevada (Goff et al. 2002, 88766). Figure 4.3-2 shows a comparison of "same-site" data analyzed by UWM and the U.S. Geological Survey (USGS) in Reston, Virginia. In this case, these data are generated from splits of the same water samples. Repeatedly, the UWM data are skewed roughly by the same amount as in Figure 4.3-1. However, the UWM data in both cases appear to be internally consistent, which are precise but not accurate. The trends and general characteristics of the data are similar, but, because they are skewed, the data are not comparable with data reported by other analytical laboratories.

Because of this problem, EES Division personnel decided to compare the results of numerous external laboratories performing stable isotope analyses on water samples. A large quantity of cold meteoric water was collected from S-Site (TA-16) and placed in a Teflon-lined, sealed, 55-gal. drum. Double or triple aliquots of this water were then sent to the following laboratories for analysis: Global, Geochron, New Mexico Technical Institution (NMTI), U.S. Geological Survey, University of Miami, University of New Mexico (UNM), and UWM. Three laboratories (Geochron, U.S. Geological Survey, and University of Miami) produced results that straddle the World Meteoric Water Line (WMWL) and the Jemez Mountains Meteoric Water Line (JMWL) (Figure 4.3-3) (Craig 1961, 88748; Vuataz and Goff 1986, 73687). These data provide the most reasonable results, considering previous analytical results for the springs (Figure 4.3-1). Because these were cold meteoric waters, it was impossible to evaluate which of these three laboratories was the most precise and accurate without performing additional analyses and thoroughly evaluating each laboratory's analytical procedures and methods. Stable isotope analyses are now performed by EES-6, producing appropriate QA, as required by the ENV-ERS Program.

In contrast, UWM data are considerably different than analytical data from the other laboratories, having higher  $\delta$ D values and lower  $\delta^{18}$ O values. Analytical results provided by UNM are slightly skewed to higher δD values, but stable isotope data reported by Global and NMTI are skewed to lower δD and higher  $δ<sup>18</sup>O$ values, respectively. It appears that each of the laboratories produces internally consistent data; however, the data do not compare well with analytical results provided by the other laboratories.

Stable isotope data reported from Geochron, U.S. Geological Survey, and University of Miami are most representative of the Pajarito Plateau and Sierra de los Valles. Stable isotope analyses for geochemical and hydrologic evaluation of groundwater for Laboratory sites may be compared to background and water derived from meteoric sources during environmental investigations.

## **4.3.2 Analytical Comparisons: Tritium Analyses Performed by the University of Miami and Teledyne**

Hydrologic and geochemical information regarding groundwater residence times and flow paths are obtained by performing tritium analyses on water samples. The half-life for tritium is 12.33 yr, and this isotope decays by emission of a β particle (electron) to helium (<sup>3</sup>He). The source and age of a particular water sample may be inferred by its tritium activity. Groundwater samples with less than 1 to 2 pCi/L generally are greater than 60 yr (Shevenell and Goff 1995, 73689) and have been isolated from recent sources of tritium, including treated Laboratory discharges and local precipitation.

The University of Miami performed tritium analyses on water samples using liquid scintillation, direct counting, and electrolytic enrichment, depending on the activity of tritium in a given sample. Electrolytic enrichment is the most sensitive method, providing an IDL of 0.5 pCi/L. Liquid scintillation is an appropriate method for water samples containing 300 pCi/L or greater of tritium. Direct counting is an appropriate method when activities of tritium range between 3.2 and 300 pCi/L.

### **4.3.2.1 Quality Assurance and Quality Control**

The quality of analytical results reported by the University of Miami was evaluated through primary and duplicate water samples, analytical method(s), analytical consistency, and data-trend analysis. Analytical results of tritium, reported by the University of Miami and Teledyne, are discussed in this section. The groundwater samples were analyzed by Teledyne during 1997 and 1998.

The primary and duplicate water samples analyzed by the University of Miami show strong agreement, characterized by an  $r^2$  value equal to 0.998, as shown in Figure 4.3-4. Figure 4.3-5 shows tritium activities reported by the University of Miami and Teledyne for the fifteen background stations sampled in 1997 and 1998. The two analytical laboratories show poor agreement. Only samples that contain activities of tritium near or at the IDL (0.5 pCi/L) compare reasonably well. Both laboratories used direct counting methods for groundwater samples containing activities of tritium greater than 3.2 pCi/L. Activities of tritium reported by the University of Miami generally are greater than those reported by Teledyne.

There is reasonable consistency in tritium activities reported by the University of Miami for several background sampling stations, as shown in Figures 4.3-6 (Apache Spring), 4.3-7 (well LAO-B), and 4.3-8 (Spring 9B). Variation in tritium activity at some sampling stations is expected because of varying tritium activities in precipitation that provide recharge to several springs within the Sierra de Los Valles (Apache Spring, Water Canyon Gallery, and upper Cañon de Valle Spring). The interlaboratory comparison also included well LAO-B (alluvial groundwater, upper Los Alamos Canyon), La Mesita Spring, Pine Spring, Seven Springs, Spring 9B, and Water Canyon Gallery. Water samples analyzed by Teledyne do not compare well with analytical results reported by the University of Miami. Tritium results provided by the University of Miami are more consistent for all of the springs sampled as part of this investigation.

Water samples collected during this investigation were submitted to the University of Miami for analysis and underwent QA/QC analysis. The tritium analytical results reported by the University of Miami are of high quality, and they are consistent over time for each background sampling station. These factors help make the University of Miami data technically defensible. Reasonable decisions regarding groundwater flow paths, residence times, and the presence or absence of tritium can be made using these University of Miami data.

### **4.3.3 Analytical Comparisons: Uranium Analyses Performed by Paragon Analytics, Inc. and General Engineering Laboratories**

An analytical method for aqueous uranium requires a low IDL of less than 1  $\mu$ g/L because dissolved background concentrations of this analyte typically are lower than this level in groundwater at the Laboratory. Paragon Analytics, Inc. performed uranium analyses on groundwater samples using LIKPA, which has an IDL of 0.1 µg/L. GEL analyzes uranium by using the ICPMS method, which provides a similar IDL. The LIKPA method was available before the use of ICPMS during this investigation. LIKPA is a viable analytical method, provided that the ionic strength of the solution is less than 0.7 molal and that dissolved concentrations of chloride are less than 1000 mg/L. However, elevated concentrations of chloride, especially in solid samples, produce interference that biases the results. Groundwater samples collected during this investigation and analyzed for uranium using the LIKPA method have chloride concentrations of less than 20 mg/L.

Figure 4.3-9 shows distributions of dissolved uranium within background spring and well samples analyzed by both LIKPA and ICPMS for the late 1999 and early 2000 sampling round. The correlation is excellent with an  $r^2$  value equal to 1.0, suggesting that for the Laboratory background water samples both methods produce high-precision and accurate analytical results. Concentrations of dissolved uranium analyzed by ICPMS at most background-sampling stations are less than 1 µg/L. This result is consistent

with the other sampling rounds conducted in 1997 and 1998. In summary, both LIKPA and ICPMS provided consistent analytical results for uranium, and results for all analyses are suitable for use to determine statistical distributions of this analyte. Based on these comparisons, it was determined that both GEL and Paragon Analytics, Inc. provided acceptable results; these data have been incorporated into the data set.

## **4.3.4 EES-6 Screening Analyses for Inorganic Analytes**

This section and Appendix F present a summary of the procedures, methods, and equipment used by EES-6 for analyzing groundwater samples collected as part of this investigation. Analyses of major cations and anions and trace elements were performed by EES-6. A summary of interlaboratory comparisons of chemical data for inorganic analytes performed by EES-6, Paragon Analytics, Inc., and other contract laboratories for the NMED Oversight Bureau (OB) is also presented. The EES-6 aqueous chemistry laboratory provided analytical results for groundwater and surface water samples, which are used for screening purposes to make decisions in the field. These screening data are supported by validated laboratory analytical results external to the Laboratory.

The EES-6 analytical laboratory uses methods developed from EPA, SW 846 (EPA 1987, 31732) for analyzing inorganic chemicals in aqueous solutions. Laboratory standards, blanks, duplicates, blind samples, and National Institute of Standards and Testing (NIST) reference waters are run as part of the QA and QC programs. Analytical results from EES-6 compare very well with those provided by Paragon Analytics, Inc. ENV-ERS Program has approved the EES-6 laboratory for providing high-precision data for anions and metals and fully validated QA/QC stable isotopes.

## **4.3.4.1 Analytical Comparisons**

Splits of groundwater samples were collected by the NMED-OB during this investigation and analyzed at external laboratories. Shortly after sampling, Laboratory personnel delivered groundwater samples to EES-6 for chemical analyses and also shipped samples to Paragon Analytics, Inc. and other ENV-ERS Program laboratories. Paragon Analytics, Inc. performed chemical and radiochemical analyses on the groundwater samples collected as part of this investigation. Paragon Analytics, Inc. uses the ICPAES method for metal and trace-element analyses, including aluminum, antimony, arsenic, barium, beryllium, boron, calcium, cadmium, cobalt, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, strontium, thallium, vanadium, and zinc. The EES-6 laboratory used AA methods for specific trace analytes, including arsenic, antimony, cadmium, cesium, chromium, cobalt, copper, lead, molybdenum, nickel, potassium, rubidium, selenium, silver, sodium, thallium, and tin. The ICPAES method was also used by EES-6 to analyze for aluminum, barium, beryllium, boron, calcium, iron, magnesium, manganese, potassium, sodium, silicon, strontium, titanium, vanadium, and zinc. Both laboratories used the CVAA method for mercury analysis. AA provides lower detection limits than ICPAES for many trace analytes and better precision for low-level sodium and potassium. The ICPMS method provides even better sensitivity for most analytes, including important analytes not normally included, such as uranium and thorium. GEL analyzed the groundwater samples collected in late 1999 and in 2000 for antimony, beryllium, cadmium, lead, thallium, and uranium, using the ICPMS method.

Appendix F provides a comparison of analytical results reported by EES-6 and Paragon Analytics, Inc. for several selected springs and alluvial well LAO-B. Apache Spring, La Mesita Spring, and Doe Spring are representative of groundwater within perched-intermediate zones (Tschicoma Formation and Cerros del Rio basalt) and the regional aquifer (Santa Fe Group sediments).

### **4.3.4.2 Summary for Inorganic Analytes**

Analytical results provided by EES-6 compare very favorably with Paragon Analytics, Inc. for major ions and most trace elements. The EES-6 screening analytical methods include ICPAES, AA, IC, and ISE. The AA method, however, provides lower IDLs for many trace elements in aqueous solution than does the ICPAES method used by Paragon Analytics, Inc. Instrument detection limits associated with ICPAES vary between laboratories, depending on the specific instrument and the configuration being used (axial vs radial view). Analytical results provided by NMED-OB and Paragon Analytics, Inc. showed some inconsistencies in IDLs inherent from the ICPAES method. Because of the favorable comparison, EES-6 data have been combined with the rest of the data since they are suitable and representative of the background geochemistry.

### **4.3.5 Summary for Stable Isotopes and Tritium**

Stable isotope data reported from Geochron, U.S. Geological Survey, and the University of Miami are most representative of the Pajarito Plateau and surrounding areas. These data, in conjunction with Laboratory site data, are used to evaluate the source and elevation of recharge water. Tritium results provided by the University of Miami are the most accurate for the background stations sampled during this investigation. These analytical results can be compared with Laboratory site data to quantitatively place a general age on water. Deep groundwaters with an activity of tritium of <1 pCi/L are greater than 60 years old. Analytical results provided by EES-6, Paragon Analytics, Inc., and GEL compare very well, and these data have been combined for alluvial groundwater, perched-intermediate groundwater, and the regional aquifer.

#### **4.4 Chemical Effects of the Cerro Grande Fire on Laboratory Background Sampling Stations**

The Cerro Grande fire significantly impacted several major watersheds that drain into and north of the Laboratory (Gallaher and Koch 2004, 88747). These include Pueblo Canyon, Los Alamos Canyon, Sandia Canyon, Mortandad Canyon, Pajarito Canyon, Water Canyon, Guaje Canyon, Rendija Canyon, and Garcia Canyon. Analytical results collected in June 2000 show that concentrations of major ions and trace elements have returned to prefire values.

A summary of a geochemical conceptual model of the impact of the Cerro Grande fire on surface water and groundwater chemistry developed by Longmire et al. (2001, 71362) is presented in this section. Ash and charcoal produced from the Cerro Grande fire consisted of complex mixtures of inorganic and organic compounds. Calcium, magnesium, silica, potassium, sodium, carbonate, manganese, iron, and other trace elements were concentrated in the ash and charcoal (Longmire et al. 2001, 71362). Longchain aliphatic, paraffin, aromatic, and polycyclic aromatic compounds were hypothesized to be concentrated in the ash and charcoal contributing to the hydrophobic nature of residual soil. Precipitation of CaCO<sub>3</sub> (calcite) resulted from the combustion of organic carbon, that oxidized to form bicarbonate and carbonate during the fire (Longmire et al. 2001, 71362). Calcite has been observed within ash samples of ponderosa pine, aspen, and scrub oak collected on the south rim of upper Los Alamos Canyon (Longmire et al. 2001, 71362). This precipitation process resulted in higher concentrations of dissolved calcium and bicarbonate in storm runoff and base flow.

During storm events, ash and charcoal were washed into canyons, carried downstream, and redeposited. After the fire, TOC and DOC concentrations in surface water were elevated because of the redistribution of ash, charcoal, soot, and other forms of organic carbon concentrated in surface water (Longmire et al. 2001, 71362). Storm runoff, consisting of a mixture of rainwater, ash, charcoal, and sediment, was characterized by a calcium-potassium-bicarbonate solution having a TDS content greater than 100 mg/L

(Longmire et al. 2001, 71362); Gallaher and Koch 2004, 88747). The TDS content of the ash-rich water was higher than prefire storm runoff and base flow. By 2002, the TDS content of base flow had returned to concentrations observed during prefire conditions in several major watersheds (Gallaher and Koch 2004, 88747). The Laboratory has conducted sampling and analyses of surface water and groundwater to assess this impact within the Pueblo Canyon, Los Alamos Canyon, Mortandad Canyon, Pajarito Canyon, Cañon de Valle, and Water Canyon watersheds (Gallaher and Koch 2004, 88747).

## **4.4.1 Analytical Results for Selected Springs and Well LAO-B**

Results of analyses for Apache Spring, Water Canyon Gallery, Pine Spring, and upper Cañon de Valle Spring are provided in Table 4.4-1. Apache Spring, Water Canyon Gallery, and upper Cañon de Valle Spring do not appear to have been impacted by the Cerro Grande fire, based on similarities in water chemistry (major ion and trace element) before and after the fire. Pine Spring, however, may have been impacted by ash-rich runoff, resulting in elevated concentrations of major ions, most notably calcium, sulfate, carbonate alkalinity, and TDS (Figure 4.4-1), and selected trace elements, including manganese (Figure 4.4-2).

Concentrations of manganese increased at Pine Spring immediately after the fire in response to increasing DOC. Organic carbon is a strong reducing agent (electron donor), that has the capacity to reduce many solutes, including manganese, iron, nitrate, sulfate, and uranium (Langmuir 1997, 56037). This change in redox chemistry resulting from the fire increased the solubility of manganese oxides and (oxy)hydroxides. Under oxidizing conditions, manganese(III, IV) is stable as MnOOH and manganese oxide, but under reducing conditions, these solids dissolve to form soluble  $Mn^{2+}$ . The aqueous chemistry observed at Pine Spring during June 2000 is expected to return to prefire conditions, depending on the residual amount of ash, charcoal, and other organic material derived from the Cerro Grande fire. Elevated concentrations of dissolved manganese in surface water (base flow) have been observed elsewhere upstream of the Laboratory (in Los Alamos Canyon and Pajarito Canyon) since the fire (Gallaher and Koch 2004, 88747). Sampling of Water Canyon Gallery by the Laboratory since the fire, however, has shown that this sampling station has returned to pre-Cerro Grande fire conditions with respect to major ions and trace elements.

The June 2000 analytical results for Apache Spring, Water Canyon Gallery, upper Cañon de Valle Spring, and Pine Spring were not included in the statistical analysis for the background data set because impacts from the Cerro Grande fire were observed. Continued sampling of these springs is necessary to evaluate their long-term trends in water chemistry.

Well LAO-B was not directly affected by the Cerro Grande fire. However, upper Los Alamos Canyon west of the well was severely impacted. Ash present in runoff recharged alluvial groundwater in the canyon that resulted in iron and manganese reduction, elevated concentrations of major cations and anions and trace elements in several water sheds (Gallaher and Koch 2004, 88747). Prefire conditions have been restored at the well, however, based on the analytical results for major ions (excluding calcium and magnesium), trace anions (fluoride), excluding trace elements largely collected from June 2000 through May 2002 (LANL 2004, 87390).

### **5.0 SUMMARY AND CONCLUSIONS**

#### **5.1 Summary**

A hydrogeochemical investigation of background subsurface waters has been conducted for the Laboratory. This data set provides the most robust and integrated chemical and statistical analyses of background subsurface water chemistry conducted for the Laboratory. This included a comprehensive field, chemical, radiochemical, isotopic, and statistical investigation of 15 sampling stations within the Pajarito Plateau/Jemez Mountains region from 1997 to 2000. Groundwaters from alluvium, Bandelier Tuff (Otowi Member and Guaje Pumice Bed), Tschicoma Formation, Cerros del Rio basalt, hydromagmatic deposits, Totavi gravels, and Santa Fe Group sediments were sampled, analyzed, and evaluated as part of this investigation. The sampling sites for this investigation were chosen to provide background data for groundwater occurring in shallow alluvium (well LAO-B and Pine Spring), perched-intermediate aquifers within volcanic rocks (Seven Springs, Apache Spring, Water Canyon Gallery, upper Cañon de Valle Spring, and well LAOI(A)-1.1), and the regional aquifer (Doe Spring, Spring 9B, Pajarito Spring, Spring 1, La Mesita Spring, Sacred Spring, and wells Otowi-4 and Guaje-5). Pajarito Spring (Spring 4A) and La Mesita Spring are separated from the other 13 sampling sites for statistical analyses because Pajarito Spring contains nitrate (as nitrogen) (1 mg/L) and perchlorate (0.5  $\mu$ g/L), and La Mesita Spring is part of a different hydrogeochemical system representative of the Rio Grande Valley. Representative background samples were collected, analyzed, and statistically evaluated from the remaining 13 stations.

The overall objectives of this study were fulfilled and included

- reviewing available background hydrogeochemical data collected at the Laboratory and surrounding areas before 1997;
- collecting additional groundwater samples from background stations (springs and wells) for alluvial and perched-intermediate groundwater and the regional aquifer; and
- providing validated analytical results and statistical distributions for the different analytes (pre-1997 and post-1997) occurring within alluvial, perched-intermediate groundwater, and the regional aquifer.

Results of statistical analyses, including minimum, mean, median, maximum, one standard deviation, and coefficient of variation, are provided for the alluvium (Tables 4.2-2a through 4.2-2g), perched-intermediate zones (Tables 4.2-3a through 4.2.3g), the regional aquifer (Tables 4.2-4 a through 4.2-4g), La Mesita Spring (Tables 4.2-5a through 4.2-5g), and Pajarito Spring (Tables 4.2-6a through 4.2-6g). The tables containing results of statistical analyses are grouped by filtered and nonfiltered samples for each aquifer type. Other parameters, including the number of samples and number of detects and nondetects, are also provided in the tables. The pre-1997 and post-1997 chemical data are both reported separately and combined for statistical analyses. The post-1997 data are more representative of background water chemistry for the three aquifer types because analytical instruments used during analyses have lower IDLs compared to those used for the pre-1997 analyses. IDLs for antimony, beryllium, cadmium, lead, thallium, and uranium were higher for the pre-1997 samples than those for the post-1997 samples. Analytical methods consisting of GFAA, HAA, and ICPMS provide lower IDLs compared to ICPAES for these trace elements. The IDLs for the post-1997 samples are recommended when comparisons are conducted between background and site data. Table 4.2-2e (alluvial groundwater), Table 4.2-3e (perched-intermediate volcanic rock), and Table 4.2-4e (regional aquifer) are recommended for evaluating the statistical properties of background concentrations of solutes within the three aquifer types.

## **5.2 Geochemical Variations within Groundwater Types**

Important physical, geochemical, and statistical attributes of alluvial and perched-intermediate groundwater and the regional aquifer are summarized in this subsection.

- Groundwater temperature increases with depth from the alluvium to the regional aquifer in response to ambient and Jemez Mountains geothermal gradients. Temperature measurements of groundwater are very useful in differentiating perched-intermediate systems from the regional aquifer.
- The three aguifer types are characterized by a pH range from 6.0 to 9.2, with the greatest variation within perched-intermediate groundwaters. The most basic pH measurements were associated with the perched-intermediate groundwaters.
- Concentrations of calcium, magnesium, sodium, and potassium are the lowest within the alluvial groundwater and highest in the regional aquifer. The range of major cation concentrations is the lowest for the alluvial system and the highest in the regional aquifer. The same compositional and statistical trends are observed for the major anions chloride, sulfate, and bicarbonate within the three aquifer types.
- Concentrations of nitrate (as nitrogen) and fluoride are the lowest within the alluvial system, increase in the perched-intermediate system, and are the highest within the regional aquifer. Concentrations of nitrate (as nitrogen) are <0.6 mg/L in groundwater beneath the Pajarito Plateau and are greater than 1 mg/L at Spring 1 in White Rock Canyon near the confluence with lower Los Alamos Canyon.
- Perched-intermediate groundwater contains the greatest range of fluoride concentrations.
- Background concentrations of arsenic, barium, boron, bromide, strontium, and uranium were the lowest within alluvial groundwater and the highest within the regional aquifer. The highest concentrations of dissolved arsenic (3.7 to 4.4 µg/L) were measured at Spring 1. Concentrations of these trace elements within the perched-intermediate system were between the low and high ends.
- Background concentrations of uranium are remarkably uniform  $\langle$ <0.6  $\mu$ g/L) in the regional aquifer beneath the Pajarito Plateau and substantially increase at Spring 1 and La Mesita Spring.
- Background/fallout activities of tritium are the highest for the Sierra de los Valles springs and alluvial groundwater (well LAO-B and Pine Spring) and the lowest within the regional aquifer (less than 3 pCi/L). This finding indicates the age of groundwater is increasing from shallow to deep systems.

## **5.3 Uncertainties**

A comprehensive investigation of groundwater chemistry, hydrostratigraphy of sampling sites, and detailed statistical analyses has been conducted. A high degree of confidence lies within the background water chemistry data as a result of this investigation. However, several uncertainties should be taken into consideration in light of the conclusions of this study.

1. The detailed lithology, the criteria for stratigraphic divisions, and the nomenclature of sedimentary units beneath the Pajarito Plateau retain many uncertainties (i.e., compare the highly contrasting stratigraphy of Purtymun 1995, 45344, to that of Goff et al. 2002, 88776). Because units such as the Puye Formation, Totavi Lentil, and various subunits within the Santa Fe Group host or partially host the regional aquifer, an improved geologic framework is needed to reduce uncertainty in the hydrostratigraphy of the Santa Fe Group.

- 2. As the geochemical and geohydrologic conceptual models continue to evolve, uncertainty is likely to decrease in groundwater flow paths, solute and groundwater residence times, age(s) of deep groundwater, and hydrogeochemical processes that control groundwater composition.
- 3. Uncertainties exist about the complete representative nature of groundwater chemistry within the alluvium with currently only two background sampling stations.
- 4. The data collected from wells and springs during this investigation generally reflect background, excluding Pajarito Spring (Spring 4A). However, the long-term (50 yr and more) chemical composition of background sampling sites within and downgradient of the Laboratory is likely to evolve over many decades.

#### **5.4 Conclusions**

Hydrogeochemical data and hydrogeologic information collected during the background investigation satisfy the Consent Order requirement, Section IV.A.3.d, which stipulates that the Respondents shall determine the background concentrations for naturally occurring metals and general chemistry parameters in alluvial, intermediate, and regional groundwater. This background investigation report states the background concentration for each metal and the general chemistry parameters, and states the bases for selecting each such concentration. Background distributions of solutes presented in this report are applicable to Laboratory site evaluation. Results of this investigation, including hydrostratigraphic descriptions, multiple chemical analyses, and statistical evaluations provide a technically defensible background database for 13 of the 15 subsurface waters for the Pajarito Plateau and Sierra de los Valles. Table 4.2-2e (alluvial groundwater), Table 4.2-3e (perched-intermediate volcanic rock), and Table 4.2-4e (regional aquifer) are recommended for evaluating the statistical properties of background concentrations of solutes within the three aquifer types.

The hydrogeologic framework and its relationship to the 15 sampling sites have been established and provide a much improved, but incomplete, understanding of hydrostratigraphy for the Pajarito Plateau and surrounding areas west of the Rio Grande. Detailed descriptions of the location, physical characteristics, and hydrogeology of the 15 sampling sites have expanded an understanding of the spatial variability of the three aquifer types.

Quantifying the relationship between groundwater chemistries and aquifer materials (alluvium, perchedintermediate volcanics, and the regional aquifer) has advanced the conceptual Laboratory-specific hydrogeochemical model. For example, increasing solute concentrations, in addition to TDS and specific conductance, occurs from alluvial groundwater, to perched-intermediate groundwater, to the regional aquifer. Increasing groundwater residence times enhance water-rock interactions, including precipitation/dissolution and adsorption/desorption reactions, which produce increasing concentrations of major ions and trace elements within the regional aquifer.

Comprehensive statistical analyses of the groundwater samples have advanced the understanding of solute distributions within the three aquifer types. Many of the major ions are log-normally distributed, which is a direct function of mineralogy of aquifer material, groundwater chemistry, microbial populations, and solute and groundwater residence times.

Statistical parameters describing distributions of trace elements, including antimony, beryllium, cadmium, lead, and thallium, are complex because of the high percentage of nondetects. These metals generally are not leachable from silicate and oxide minerals under circumneutral pH conditions.

The short-term effects of the Cerro Grande fire on several of the background sampling sites within the Sierra de los Valles (Apache Spring, Water Canyon Gallery, upper Cañon de Valle Spring, and Pine Spring) and upper Los Alamos Canyon (well LAO-B) have been assessed. Groundwater chemistry has returned to prefire conditions at the two most impacted background sampling stations (well LAO-B and Pine Spring).

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**Figure 1.2-1. Location of fifteen sampling sites in the Jemez Mountains and near Los Alamos National Laboratory, New Mexico** 



**Figure 2.1-1. Regional and tectonic setting of the Jemez Mountains, Valles Caldera, and Pajarito Plateau in relation to the Rio Grande Rift, Española Basin, Colorado Plateau, and the Sangre de Cristo Mountains, New Mexico** 



**Figure 2.1-2. Diagram showing generalized geologic relations beneath the Pajarito Plateau. O-1 is well Otowi-1, O-4 is well Otowi-4, and R-31 refers to well R-31. Ma refers to millions of years before the present.** 



**Figure 2.1-3. Regional geologic map (Broxton and Vaniman 2005, 88707)** 



**Figure 2.1-4. Revised stratigraphy of the Pajarito Plateau (Broxton and Vaniman 2005, 88707)** 



- Wet canyons:
	- Source of recharge to intermediate groundwater and main aquifer
- Intermediate groundwater:
	- Significant contaminant transport path
	- Source of recharge to main aquifer
	- Occurs in larger canyon systems
	- Exists beneath canyons, not mesas?
	- Laterally extensive near Jemez Mountains?
	- Controlled by subsurface lithology

## **Figure 2.1-5. Hydrologic conceptual model for the canyons of the Pajarito Plateau (LANL 1998, 59599)**



## **Figure 2.1-6. Regional water-level map in the vicinity of the Pajarito Plateau (Robinson et al., 2005, 88767)**







**Figure 2.2-2. Average concentrations of selected trace elements within alluvial and perchedintermediate groundwater and the regional aquifer** 



**Figure 2.2-3. Results of uranium(VI) speciation calculations for Spring 9B using the computer program MINTEQA2, White Rock Canyon. Log U(VI) = -9.26 molal (m),**   $log F = -4.69$  m,  $log H_4SiO_4 = -2.92$  m, and  $log CO_3^{2-} = -3.07$  m at 20.5°C.



**Figure 2.2-4. Saturation indices for calcite versus calcium and bicarbonate concentrations in Laboratory background springs and wells** 



**Figure 2.2-5. Activity diagram of log[H4SiO4] versus log activity (Ca<sup>2</sup> +/[H+]<sup>2</sup> ) at 25**°**C for wells Otowi-4, R-9, R-12 (screen #3), LAOI(A)-1.1, and La Mesita Spring** 



**Figure 4.2-1. Comparison of field replicate (dup.)samples ("plus" symbols are nonfiltered samples, and squares are filtered samples)** 



**Figure 4.2-1 (continued) Comparison of field replicate (dup.)samples ("plus" symbols are nonfiltered samples, and squares are filtered samples)** 



 $NO<sub>3</sub>$  [dup.] = 0.06 + 0.91\* $NO<sub>3</sub>$ ,  $r<sup>2</sup>$  = 0.99, n = 15

**Figure 4.2-1. (continued) Comparison of field replicate (dup.)samples ("plus" symbols are nonfiltered samples, and squares are filtered samples)** 



**Figure 4.2-2. Comparison of water chemistry results for analytical laboratories and methods ("plus" symbols are nonfiltered samples, and squares are filtered samples)** 



**Figure 4.2-2. (continued) Comparison of water chemistry results for analytical laboratories and methods ("plus" symbols are nonfiltered samples, and squares are filtered samples)** 



EES = Earth and Environmental Sciences CL = contract laboratory LIKPA= laser-induced kinetic phosphorometric analysis ICPMS = inductively coupled plasma mass spectrometry UM = University of Miami

## **Figure 4.2-2. (continued) Comparison of water chemistry results for analytical laboratories and methods ("plus" symbols are nonfiltered samples, and squares are filtered samples)**



WMWL = worldwide meteoric water line JMWL = Jemez meteoric water line

#### **Figure 4.3-1. Comparison of archived stable isotope data with University of Western Michigan 1997 data**



WMWL = worldwide meteoric water line DMWL = Dixie Valley meteoric water line





WMWL = worldwide meteoric water line JMWL = Jemez meteoric water line

#### **Figure 4.3-3. Comparative stable isotope results from Los Alamos National Laboratory internal standard**



**Figure 4.3-4. Comparison of primary and duplicate water samples analyzed for tritium by the University of Miami, Los Alamos National Laboratory background sites, 1997–1998** 



**Figure 4.3-5. Comparison of tritium results reported by the University of Miami and Teledyne for Los Alamos National Laboratory background groundwater samples collected from April through October, 1998** 



**Figure 4.3-6. Comparison of tritium results reported by the University of Miami and Teledyne for Apache Spring; (left to right) groundwater samples were collected during May 7, 1997, August 6, 1997, August 6, 1997 (dup.), February 9, 1998, and July 1, 1998** 



**Figure 4.3-7. Comparison of tritium results reported by the University of Miami and Teledyne for LAO-B well; (left to right) groundwater samples collected during May 14, 1997, August 1, 1997, August 1, 1997 (dup.), February 24, 1998, and October 2, 1998**



**Figure 4.3-8. Comparison of tritium results reported by the University of Miami and Teledyne for Spring 9B; (left to right) groundwater samples collected during April 22, 1997, August 18, 1997, February 3, 1998, and September 23, 1998, and January 7, 2000** 



**Figure 4.3-9. Comparison of dissolved uranium analyzed by laser-induced kinetic phosphorimetric analysis and inductively coupled plasma mass spectrometry for LANL background sampling stations, December 1999 and January 2000** 



**Figure 4.4-1. Concentrations of total dissolved solids and major ions at Pine Spring, Garcia Canyon (alluvium, Puye Formation, and lavas of the Polvadera Group)** 



**Figure 4.4-2. Concentrations of dissolved aluminum, iron, manganese, and strontium at Pine Spring, Garcia Canyon (Puye Formation and lavas of the Polvadera Group)** 





*Source*: Goff et al. 2002, 88776.

<b>Type of Data</b>	Available Data (Pre-1997)	Data Required (1997-2000)
<b>Water-quality</b> data	Analyses of groundwater samples are available from Laboratory surveillance and geothermal programs, ER Project, DOE-OB studies, NURE* Project, consultant reports, and the U.S. Geological Survey.	Analyses of additional groundwater samples representing each mode of groundwater occurrence.
<b>Sample</b> handling (filtered/ nonfiltered)	Available data from filtered samples are adequate for use. However, nonfiltered samples that have been collected by some previous programs have greater errors for the cation-anion charge balance than $\pm$ 10%; therefore, they are not of adequate quality.	Analyses of filtered and nonfiltered samples (low turbidity), except for total suspended solids, which require a nonfiltered sample.
<b>Analytes</b>	Assessment of the pre-1997 data set (of 55 filtered samples) shows good agreement between cation sum and anion sum. Ten samples had laboratory duplicates and the laboratory variation is less than 20% relative standard deviation. Therefore, these data can be used in the establishing background. However, most of the major cations and anions are frequently detected, but many of the trace elements have low detection rates. The number of analytes has varied annually at each spring or well.	Major cations (Ca, Mg, Na, and K); major anions (HCO <sub>3</sub> , CI, and SO <sub>4</sub> ); trace elements (Ag, AI, As, B, Ba, Be, Br, Cd, ClO <sub>3</sub> , Co, Cr, Cs, Cu, F, Fe, Hg, I, Li, Mn, Mo, NH <sub>4</sub> , Ni, NO <sub>2</sub> , NO <sub>3</sub> , Pb, PO <sub>4</sub> , Rb, Sb, Se, $S_2O_3$ , Sn, Sr, Ti, Tl, U, V, and Zn); SiO <sub>2</sub> ; total dissolved solids, fallout radionuclides $(^{241}$ Am, $^{137}$ Cs, <sup>238</sup> Pu, <sup>239,240</sup> Pu, <sup>90</sup> Sr, <sup>3</sup> H, <sup>234</sup> U, <sup>235</sup> U, and <sup>238</sup> U); dissolved organic carbon, and stable isotopes ( $\delta^{18}O$ , $\delta^{15}$ N, and $\delta$ D).
Analytical methods	Samples analyzed by EPA SW 846 and other analytical methods are acceptable for use in determining background water chemistry. These include ICPOES, ICPMS, IC, alkalinity titration, alpha spectrometry, gamma spectroscopy, direct counting, electrolytic enrichment, and IRMS.	SW 846 and other EPA methods for inorganic analytes by ICPAES, ICPMS, CVAA, AA, IC, and colorimetry. Analysis of fallout radionuclides by alpha spectrometry, gamma spectrometry, liquid scintillation, gases proportional counting, electrolytic enrichment/gas proportional counting. Field parameters include temperature, pH, specific conductance, turbidity, and carbonate alkalinity.

**Table 3.1-1 Data Input Requirements for Laboratory Background Hydrogeochemistry Investigation** 

\*NURE – National uranium resource evaluation.





<b>Sample Station</b>	<b>Date</b> MM/DD/YY	Temperature $(^{\circ}C)$	<b>Specific</b> Conductance $(\mu S/cm)$	pHa	<b>Turbidityb</b> (NTU)
Doe Spring, filtered	04/22/97	17.5	125L <sup>c</sup>	8.19	d
Doe Spring, nonfiltered	04/22/97	17.5	124L	8.19	
Spring 9B, filtered	04/22/97	20.1	122L	7.82	
Spring 9B, nonfiltered	04/22/97	20.1	122L	7.82	
Pajarito Spring, filtered	04/27/97	21.3	207	7.30	5
Pajarito Spring, nonfiltered	04/27/97	21.3	207	7.30	5
Seven Springs, filtered	04/27/97	12.4	83	7.49	$\mathbf 0$
Seven Springs, nonfiltered	04/27/97	12.4	83	7.49	0
Pine Spring, filtered	05/07/97	6.8	100	5.81	0
Pine Spring, nonfiltered	05/07/97	6.8	100	5.81	0
Apache Spring, filtered	05/07/97	8.3	199	7.27	0
Apache Spring, nonfiltered	05/07/97	8.3	199	7.27	$\mathbf 0$
Water Canyon Gallery, filtered	05/07/97	11.3	104	7.42	$\pmb{0}$
Water Canyon Gallery, nonfiltered	05/07/97	11.3	104	7.42	$\mathbf 0$
LAOI(A)-1.1, filtered	05/09/97	9.7	114	6.82	0
LAOI(A)-1.1, nonfiltered	05/09/97	9.7	114	6.82	0
LAOI(A)-1.1, filtered, duplicate	05/09/97	9.7	114	6.82	$\Omega$
Upper Cañon de Valle, filtered, duplicate	05/13/97	8.9	70	7.33	0
Upper Cañon de Valle, filtered	05/13/97	8.9	70	7.33	$\mathbf 0$
Upper Cañon de Valle, nonfiltered	05/13/97	8.9	70	7.33	0
LAO-B, filtered	05/14/97	4.8	105	6.64	0
LAO-B, nonfiltered	05/14/97	4.8	105	6.64	0
Spring 1, filtered	05/21/97	16.8	218	7.43	0
Spring 1, nonfiltered	05/21/97	16.8	218	7.43	0
La Mesita, filtered	05/21/97	15.2	285	7.17	$\pmb{0}$
La Mesita, nonfiltered	05/21/97	15.2	285	7.17	
Otowi 4, filtered	05/29/97	27.9	306	6.92	
Otowi 4, nonfiltered	05/29/97	27.9	306	6.92	
Otowi 4, filtered, duplicate	05/29/97	27.9	306	6.92	
Guaje 5, filtered	05/29/97	26.8	186	7.86	
Guaje 5, nonfiltered	05/29/97	26.8	186	7.86	
Guaje 5, filtered, duplicate	05/29/97	26.8	186	7.86	
Sacred Spring, filtered	05/29/97	14.3	225	7.53	0
Sacred Spring, nonfiltered	05/29/97	14.3	225	7.53	0
LAO-B, filtered	08/01/97	9.6	98	6.79	1
LAO-B nonfiltered	08/01/97	9.6	98	6.79	1

**Table 3.2-1 Summary of Field Parameters Measured at LANL Background Sampling Stations, 1997–2000** 



# **Table 3.2-1 (continued)**

<b>Sample Station</b>	<b>Date</b> MM/DD/YY	Temperature $(^{\circ}C)$	<b>Specific</b> Conductance $(\mu S/cm)$	pH	<b>Turbidity</b> (NTU)
Apache Spring, nonfiltered	02/09/98	6.5	165	7.96	5.0
Pine Spring, filtered	02/10/98	3.6	70	6.78	41.7
Pine Spring, nonfiltered	02/10/98	3.6	70	6.78	41.7
Seven Springs, filtered	02/10/98	10.5	120	7.50	2.2
Seven Springs, nonfiltered	02/10/98	10.5	120	7.50	2.2
Pajarito Spring, filtered	02/18/98	18.8	200	7.83	1.6
Pajarito Spring, nonfiltered	02/18/98	18.8	200	7.83	1.6
Pajarito Spring, duplicate	02/18/98	18.8	200	7.83	1.6
Upper Cañon de Valle, filtered	02/23/98	6.7	80	8.04	1.4
Upper Cañon de Valle, nonfiltered	02/23/98	6.7	80	8.04	1.4
LAO-B, filtered	02/24/98	4.4	90	6.91	4.1
LAO-B, nonfiltered	02/24/98	4.4	90	6.91	4.1
LAOI(A)-1.1, filtered	02/25/98	8.7	100	6.68	27.2
LAOI(A)-1.1, nonfiltered	02/25/98	8.7	100	6.68	27.2
Guaje 5, filtered (not sampled)					
Guaje 5, nonfiltered (not sampled)					
Otowi 4, filtered	02/26/98	26.1	290	7.58	1.4
Otowi 4, nonfiltered	02/26/98	26.1	290	7.58	1.4
Spring 1, filtered	04/07/98	15.6	215	7.99	5.4
Spring 1, nonfiltered	04/07/98	15.6	215	7.99	5.4
La Mesita Spring, filtered	04/07/98	12.5	320	7.40	7.6
La Mesita Spring, nonfiltered	04/07/98	12.5	320	7.40	7.6
NMED Sacred Spring Source, filtered	04/14/98	11.6	250	7.24	3.2
NMED Sacred Spring Source, nonfiltered	04/14/98	11.6	250	7.24	3.2
Sacred Spring, nonfiltered	04/14/98	9.3	180	7.36	2.2
Sacred Spring, filtered, duplicate	04/14/98	9.3	180	7.36	2.2
Upper Cañon de Valle, filtered	07/01/98	$7.3$	65	7.76	4.6
Upper Cañon de Valle, nonfiltered	07/01/98	7.3	65	7.76	4.6
Apache Spring, filtered	07/01/98	9.1	130	7.32	23.8
Apache Spring, nonfiltered	07/01/98	9.1	130	7.32	23.8
Pajarito Spring, filtered	07/06/98	20.6	160	7.97	0.4
Pajarito Spring, nonfiltered	07/06/98	20.6	160	7.97	0.4
Seven Springs, filtered	07/06/98	10.7	100	7.51	2.7
Seven Springs, nonfiltered	07/06/98	10.7	100	7.51	2.7
Spring 1, filtered	07/07/98	17.6	190	7.81	2.6
Spring 1, nonfiltered	07/07/98	17.6	190	7.81	2.6
Spring 1, filtered, duplicate	07/07/98	17.6	190	7.81	2.6
La Mesita Spring, filtered	07/07/98	15.0	230	7.48	9.3
La Mesita Spring, nonfiltered	07/07/98	15.0	230	7.48	9.3
La Mesita Spring, filtered, duplicate	07/07/98	15.0	230	7.48	9.3

**Table 3.2-1 (continued)** 




<b>Sample Station</b>	Date <b>MM/DD/YY</b>	Temperature (°C)	<b>Specific</b> Conductance $(\mu S/cm)$	рH	<b>Turbidity</b> (NTU)
Otowi 4, filtered (not sampled)					
Otowi 4, nonfiltered (not sampled)					
LAOI(A)-1.1, filtered	04/13/00	11.9	70	6.85	12.8
LAOI(A)-1.1, nonfiltered	04/13/00	11.9	70	6.85	12.8
Spring 9B, filtered	04/06/00	20.0	100	6.44	0.7
Spring 9B, nonfiltered	04/06/00	20.0	100	6.44	0.7
Water Canyon Gallery, filtered	03/30/00	11.3	70	7.4	1.2
Water Canyon Gallery, nonfiltered	03/30/00	11.3	70	7.4	1.2
Water Canyon Gallery, duplicate	03/30/00	11.3	70	7.4	1.2
Water Canyon Gallery, nonfiltered	03/30/00	11.3	70	7.4	1.2
Apache Spring, filtered	03/29/00	7.6	270, 290 <sup>e</sup>	7.33	7.3
Apache Spring, nonfiltered	03/29/00	7.6	270, 290 <sup>e</sup>	7.33	7.3
Pine Spring, filtered	03/30/00	6.8	70, 70 <sup>e</sup>	6.69	44.9
Pine Spring, nonfiltered	03/30/00	6.8	70, 70 <sup>e</sup>	6.69	44.9
Pine Spring, filtered	03/30/00	6.8	70, 70 <sup>e</sup>	6.69	44.9
Pine Spring, nonfiltered	03/30/00	6.8	70, 70 <sup>e</sup>	6.69	44.9
Seven Springs, filtered	03/29/00	10.8	110, 110 <sup>e</sup>	7.22	3
Seven Springs, nonfiltered	03/29/00	10.8	110, 110 <sup>e</sup>	7.22	3
Pajarito Spring, filtered	03/31/00	20.6	200, 220 $^{\circ}$	7.99	3
Pajarito Spring, nonfiltered	03/31/00	20.6	200, 220 $^{\circ}$	7.99	3
Pajarito Spring, filtered, duplicate	03/31/00	20.6	200, 220 $^{\circ}$	7.99	3
Pajarito Spring, nonfiltered, duplicate	03/31/00	20.6	200, 220 $^{\circ}$	7.99	3
Upper Cañon de Valle, filtered	04/05/00	7.2	70	6.41	4.8
Upper Cañon de Valle, nonfiltered	04/05/00	7.2	70	6.41	4.8
LAO-B, filtered	03/24/00	3.5	78, 80 <sup>e</sup>	6.93	3
LAO-B, nonfiltered	03/24/00	3.5	78, 80 <sup>e</sup>	6.93	3
Spring 1, filtered	04/04/00	18.5	150, 150 <sup>e</sup>	7.26	10.3
Spring 1, nonfiltered	04/04/00	18.5	150, 150 $^{\circ}$	7.26	10.3
La Mesita Spring, filtered	04/10/00	15	220	6.37	4.3
La Mesita Spring, nonfiltered	04/10/00	15	220	6.37	4.3
Sacred Spring, filtered	04/10/00	16	150	6.56	2.5
Sacred Spring, nonfiltered	04/10/00	16	150	6.56	2.5

**Table 3.2-1 (continued)** 

a pH is in standard units.

b NTU = nephelometric turbidity unit.

c L denotes that specific conductance was measured in the EES-6 analytical laboratory.

d — = Not analyzed.

e Specific conductance measurements were recorded with two instruments.

## **Table 3.2-2**

## **Field Parameters and Analytes for LANL Background Hydrogeochemistry Investigation**

## **Field Parameters**

Temperature, turbidity, specific conductance, and pH

#### **Major Cations and Anions and Neutral Species**

Ca, Mg, Na, K, HCO<sub>3</sub>, carbonate alkalinity, Cl,  $SO_4$ ,  $SO_2$ , and TDS

#### **Trace Elements and DOC Fractionation**

Ag, Al, As, B, Ba, Be, Br, Cd, ClO4,Co, Cr, Cs, Cu, F, Fe, Hg, I, K, Li, Mn, Mo, NH4, Ni, NO2, NO3, Pb, PO4, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, Zn, and DOC fractionation analysis

### **Radionuclides and Stable Isotopes**

Low-detection limit tritium,  $\delta^{18}$ O,  $\delta^{15}$ N,  $\delta$ D,  $^{90}$ Sr,  $^{234}$ U,  $^{235}$ U,  $^{238}$ U,  $^{137}$ Cs,  $^{241}$ Am,  $^{238}$ Pu,  $^{239,240}$ Pu, gross alpha, gross beta, and gross gamma

Note:

TDS = total dissolved solids

DOC = dissolved organic carbon

**Table 4.1-1 Analytical Methods Used by Contract Laboratories** 

<b>Analytical Method</b>	<b>Analyte Suite</b>	<b>Analytical Laboratory</b>
ICPAES (USEPA 6010) and CVAA (USEPA 7470)	Trace metals	Paragon Analytics, Inc.
Ion chromatography (USEPA 300.0)	Anions	Paragon Analytics, Inc.
Titrimetric (USEPA 310.1)	<b>Bicarbonate</b>	Paragon Analytics, Inc.
Colorimetric (USEPA 370.1)	Dissolved silica	Huffman
Laser-induced kinetic phosphorimetry	Total uranium	Paragon Analytics, Inc.
Oxidation/Combustion (SW-415.1)	Dissolved organic carbon	Huffman
(USGS/WRI 79-4)	Dissolved organic carbon fractionation	Huffman
Alpha spectrometry	$^{241}$ Am	Paragon Analytics, Inc.
Alpha spectrometry	<sup>238</sup> Pu. <sup>239,240</sup> Pu	Paragon Analytics, Inc.
Alpha spectrometry	$^{234}$ U, $^{235}$ U, $^{238}$ U	Paragon Analytics, Inc.
Gamma spectrometry	Gamma spectrometry analytes	Paragon Analytics, Inc.
Electrolytic enrichment/Direct counting	Tritium (low-level)	University of Miami
Gas proportional counting	$90$ Sr	Paragon Analytics, Inc.

Note:

ICPAES = inductively coupled plasma atomic emission spectrometry

CVAA = cold vapor atomic adsorption

Analyte	<b>Instrument</b>	<b>EPA Method</b> Number	<b>Instrument Detection</b> Limit (ppm)
Ag	<b>GFAA</b>	200.9	0.0005
	<b>ICPAES</b>	6010	0.002
Al	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.01
As	Hydride-AA	7062	0.0002
	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.05
B	<b>ICPAES</b>	6010	0.002
Ba	<b>ICPAES</b>	6010	0.002
Be	<b>ICPAES</b>	6010	0.002
Br	IC	300	0.005
Ca	<b>ICPAES</b>	6010	0.002
Cd	<b>GFAA</b>	200.9	0.0002
	<b>ICPAES</b>	6010	0.005
CI	IC	300	0.01
CIO <sub>3</sub>	IC	300	0.02
Co	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.01
CO <sub>3</sub> /HCO <sub>3</sub> /OH	Titration	310.0	0.5
Conductivity	Electrode		0.5
Cr	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.01
Cs	<b>GFAA</b>	200.9	0.002
	AA		0.02
Cu	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.01
F	IC	300	0.01
	Electrode		0.01
Fe	<b>ICPAES</b>	6010	0.01
Hg	Cold Vapor AA	7470A	0.00002
$\mathbf{I}$	IC		0.01
Κ	AA	7610	0.01
	<b>ICPAES</b>	6010	0.2
Li	<b>ICPAES</b>	6010	0.005
Mg	<b>ICPAES</b>	6010	0.002
Mn	<b>ICPAES</b>	6010	0.002
Mo	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.02
Na	AA	7770	0.01
	<b>ICPAES</b>	6010	0.05
NH <sub>4</sub>	Electrode		0.02
Ni	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.01

**Table 4.1-2 EES-6 Analytical Instrumentation and Instrument -Detection Limits** 

Analyte	<b>Instrument</b>	<b>EPA Method</b> <b>Number</b>	<b>Instrument Detection</b> Limit (ppm)
NO <sub>2</sub>	IC	300	0.01
NO <sub>3</sub>	IC	300	0.01
Oxalate	IC	300	0.02
Pb	<b>GFAA</b>	200.9	0.002
pH	Electrode		0.01
PO <sub>4</sub>	IC	300	0.02
<b>Rb</b>	<b>GFAA</b>	200.9	0.002
	AA		0.01
Sb	Hydride AA	7062	0.0002
	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.05
Se	Hydride AA	7742	0.0002
	<b>GFAA</b>	200.9	0.002
	<b>ICPAES</b>	6010	0.1
Si	<b>ICPAES</b>	6010	0.02
Sn	<b>GFAA</b>	200.9	0.005
SO <sub>3</sub>	IC	300	0.01
SO <sub>4</sub>	IC	300	0.02
$S_2O_3$	IC		0.01
Sr	<b>ICPAES</b>	6010	0.005
Ti	<b>ICPAES</b>	6010	0.002
TI	<b>GFAA</b>	200.9	0.002
V	<b>ICPAES</b>	6010	0.002
Zn	<b>ICPAES</b>	6010	0.005

**Table 4.1-2 (continued)** 

AA - atomic absorption spectrometry

GFAA - graphite furnace atomic absorption

IC - ion chromatography

ICPAES - inductively coupled plasma atomic emission spectrometry



# **Table 4.1-3 Inorganic Target Analytes and Instrument Detection Limits Provided by Paragon Analytics, Inc.**



**Elevation from GPS instruments.** 

 $c$   $n/a$  = not applicable.  $\sigma_{\textsf{na}}$  = not available.









































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° CV = Coefficient of variation = std. dev./mean.<br>NATU = Natural uranium.<br>TUICPMS = Total uranium inductively coupled plasma mass spectrometry.<br>TULIKPA = Total uranium kinetic phosphorimetric analysis.<br><sup>d</sup> n/a = Not applic

n/a = Not applicable.

 $e$  — = No summary information, no samples analyzed.  $=$   $\sim$   $=$  No summary information, no samples analyzed. f TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium. TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium.

 $g$  Rad-gscan = gamma spectroscopy.













° CV = Coefficient of variation = std. dev./mean.<br>NATU = Natural uranium.<br>TUICPMS = Total uranium inductively coupled plasma mass spectrometry.<br>TULIKPA = Total uranium kinetic phosphorimetric analysis.<br><sup>d</sup> n/a = Not applic

n/a = Not applicable.

e — = No summary information, no samples analyzed.  $=$  No summary information, no samples analyzed.

 $f$  TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium. TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium.

 $g$  Rad-gscan = gamma spectroscopy.















° CV = Coefficient of variation = std. dev./mean.<br>NATU = Natural uranium.<br>TUICPMS = Total uranium inductively coupled plasma mass spectrometry.<br>TULIKPA = Total uranium kinetic phosphorimetric analysis.<br><sup>d</sup> n/a = Not applic

n/a = Not applicable.

e — = No summary information, no samples analyzed.  $=$  No summary information, no samples analyzed.

 $f$  TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium. TU = tritium unit, 1 TU=3.193 pCi/kg or 3.193 pCi/L tritium.

 $g$  Rad-gscan = gamma spectroscopy.











































































































































































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	Analytical Method <sup>a</sup>		Reporting Limit (ppm or mg/L)		
Analyte	EES-6	Paragon	EES-6	Paragon	
Ag	<b>GFAA</b>	<b>ICPAES</b>	0.001	0.01	
Al	<b>ICPAES</b>	<b>ICPAES</b>	0.02	0.2	
Alkalinity	Titration	Titration	1	$\mathbf{1}$	
As	Hydride-AA	<b>ICPAES</b>	0.0001	0.01	
B	<b>ICPAES</b>	<b>ICPAES</b>	0.002	Not analyzed	
Ba	<b>ICPAES</b>	<b>ICPAES</b>	0.002	0.1	
Be	<b>ICPAES</b>	<b>ICPAES</b>	0.002	0.005	
Br	IC	IC	0.01	0.01	
Ca	<b>ICPAES</b>	<b>ICPAES</b>	0.02	$\mathbf{1}$	
Cd <sup>b</sup>	<b>GFAA</b>	<b>GFAA</b>	0.001	0.005	
CI	IC	IC	0.01	0.01	
ClO <sub>3</sub>	IC	IC	0.02	Not analyzed	
Co	<b>GFAA</b>	<b>ICPAES</b>	0.002	0.01	
CO <sub>3</sub> /HCO <sub>3</sub> /OH	Titration	Titration	0.5	0.5	
Conductivity	Electrode	Electrode	0.5	0.5	
Cr	<b>GFAA</b>	<b>ICPAES</b>	0.002	0.01	
Cs	<b>GFAA</b>	<b>GFAA</b>	0.002	Not analyzed	
Cu	<b>GFAA</b>	<b>GFAA</b>	0.002	0.01	
F	IC	IC	0.01	0.01	
Fe	<b>ICPAES</b>	<b>ICPAES</b>	0.01	0.1	
Hardness	Calculated	Calculated	Calculated	Calculated	
HCO <sub>3</sub>	Titration	Titration	0.5	0.5	
Hg	Cold Vapor AA	Cold Vapor AA	0.0002	0.0002	
T	IC	IC	0.01	Not analyzed	
Κ	AA	<b>ICPAES</b>	0.01	1	
Li	<b>ICPAES</b>	<b>ICPAES</b>	0.01	Not analyzed	
Mg	<b>ICPAES</b>	<b>ICPAES</b>	0.01	$\mathbf{1}$	
Mn	<b>ICPAES</b>	<b>ICPAES</b>	0.002	0.01	
Mo	<b>GFAA</b>	<b>ICPAES</b>	0.002	0.01	
Na	AA	<b>ICPAES</b>	0.01	1	
NH <sub>4</sub>	Electrode	Electrode	0.02	0.5	
Ni	<b>GFAA</b>	<b>ICPAES</b>	0.002	0.02	
NO <sub>2</sub>	IC	IC	0.01	0.05	
NO <sub>3</sub>	IC	IC	0.01	0.05	
OH	Titration	Titration	0.5	Not analyzed	
$Pb^b$	<b>GFAA</b>	<b>ICPAES</b>	0.002	0.003	
pH	Electrode	Electrode	0.05	0.05	

**Table 4.2-7 Reporting Limits Provided by EES-6 and Paragon Analytics, Inc.** 



#### **Table 4.2-7 (continued)**

<sup>a</sup> AA = atomic absorption spectroscopy, GFAA = graphite furnace atomic absorption, IC = ion chromatography, ICPES = inductively coupled plasma atomic emission spectroscopy, ICPMS = inductively coupled plasma mass spectroscopy, LIKPA = laser-induced kinetic phosphorimetric analysis.

<sup>b</sup> ICP-MS was used for Sb, Cd, Pb, Tl, and U by the General Engineering Laboratories (GEL) for samples collected in December 1999/January 2000 and March/April 2000.

		<b>Regulatory Standard</b>			Geochemical-		
					<b>Conceptual Model</b> and Pathway	<b>Detection</b>	<b>Data</b>
Group	Analyte	<b>NMED</b>	<b>EPA</b>	<b>DOE</b>	<b>Analysis</b>	<b>Rate<sup>a</sup></b>	<b>Source</b>
Field	Temperature				X	100%	Field
	Specific conductance						
Field	(conductivity)				x	100%	Field
Field	pH	x	х		$\pmb{\mathsf{x}}$	100%	Field
Metals	Aluminum	x	X		X	29%	$CL^b$
Metals	Antimony		x		X	3%	<b>CL</b>
Metals	Arsenic	x	x		$\pmb{\mathsf{x}}$	15%	CL
Metals	<b>Barium</b>	x	x		X	97%	<b>CL</b>
Metals	Beryllium		х		X	24%	CL
Metals	Boron	x			$\pmb{\mathsf{x}}$	26%	<b>CL</b>
Metals	Cadmium	x	х		$\pmb{\mathsf{x}}$	6%	CL
Metals	Calcium				$\pmb{\mathsf{x}}$	100%	CL
Metals	Chromium, total	x	$\pmb{\mathsf{x}}$		$\pmb{\mathsf{x}}$	42%	CL
Metals	Cobalt	X	x		$\pmb{\mathsf{x}}$	19%	<b>CL</b>
Metals	Copper	x	x		X	21%	CL
Metals	Iron	x	x		$\pmb{\mathsf{x}}$	24%	CL
Metals	Lead	x	х		X	16%	CL
Metals	Magnesium				X	97%	<b>CL</b>
Metals	Manganese	x	х		$\pmb{\mathsf{x}}$	56%	CL
Metals	Mercury	x	x		$\pmb{\mathsf{x}}$	7%	CL
Metals	Molybdenum	x	x		X	15%	<b>CL</b>
Metals	Nickel	x	x		x	37%	<b>CL</b>
Metals	Potassium				$\pmb{\mathsf{x}}$	100%	CL
Metals	Selenium	x	x		X	1%	CL
Metals	Silver		х		X	4%	CL
Metals	Sodium				$\pmb{\mathsf{x}}$	100%	<b>CL</b>
Metals	Strontium				$\pmb{\mathsf{x}}$	87%	CL
Metals	Thallium		х		$\pmb{\mathsf{x}}$	19%	CL
Metals	Uranium	x	x		x	100%	<b>CL</b>
Metals	Zinc	$\pmb{\mathsf{X}}$	$\pmb{\mathsf{x}}$		X	44%	$\mathsf{CL}$
Other	Alkalinity (Lab) CaCO <sub>3</sub>				x	100%	EES <sup>c</sup>
Other	Ammonium [as N]	—			$\pmb{\mathsf{x}}$	68%	EES
Other	Bicarbonate				$\pmb{\mathsf{x}}$	100%	EES
Other	Carbon, dissolved organic				$\pmb{\mathsf{x}}$	100%	CL
Other	Chloride	x	x		$\pmb{\mathsf{x}}$	100%	<b>EES</b>
Other	Cyanide <sup>d</sup>	x	x		$\pmb{\mathsf{x}}$	na <sup>e</sup>	na
Other	Fluoride	x	x		X	100%	EES
Other	Nitrate [as N]	x	x		$\pmb{\mathsf{x}}$	91%	EES
Other	Nitrite [as N]		x		X	19%	EES
Other	Low-level perchlorate				$\pmb{\mathsf{x}}$	100%	<b>NMED</b>

**Table 4.2-8 List of Key Groundwater Analytes** 

		<b>Regulatory Standard</b>			Geochemical-		
Group	Analyte	<b>NMED</b>	<b>EPA</b>	<b>DOE</b>	<b>Conceptual Model</b> and Pathway <b>Analysis</b>	<b>Detection</b> Rate <sup>a</sup>	Data <b>Source</b>
Other	Silica				X	100%	<b>EES</b>
Other	Total dissolved solids	$\mathsf{x}$	$\mathsf{x}$		X	100%	<b>EES</b>
Other	Deuterium hydrogen ratio				X	100%	<b>CL</b>
Other	Delta deuterium				X	100%	<b>CL</b>
Other	Nitrogen-15/nitrogen-14 Ratio				x	100%	CL
Other	Oxygen-18/oxygen-16 Ratio				x	100%	<b>CL</b>
Rads	Gross alpha radiation	x	$\mathsf{x}$	$\mathsf{x}$	x	83%	CL
Rads	Americium-241			x	$\boldsymbol{\mathsf{x}}$	15%	<b>CL</b>
Rads	Plutonium-238			$\mathsf{x}$	X	8%	<b>CL</b>
Rads	Plutonium-239			x	x	9%	CL
Rads	Radium-226	x	$\boldsymbol{\mathsf{x}}$	x	X	na	na
Rads	Radium-228	x	X	x	$\boldsymbol{\mathsf{x}}$	na	na
Rads	Strontium-90	$\mathsf{x}$	х	$\mathsf{x}$	X	0%	CL
Rads	Tritium			x	$\boldsymbol{\mathsf{x}}$	100%	CL
Rads	Uranium-234			X	x	89%	<b>CL</b>
Rads	Uranium-235			x	X	25%	CL
Rads	Uranium-238			X	$\boldsymbol{\mathsf{x}}$	87%	<b>CL</b>

**Table 4.2-8 (continued)** 

<sup>a</sup> For filtered samples.

 $b$  CL = Contract laboratory.

<sup>c</sup> EES = Earth and Environmental Sciences Division (EES-6) Laboratory.<br><sup>d</sup> There is a single sample result for reactive cyanide.

e na = Not available because of lack of data.

f n.c. = Not calculated because baseline validation for University of Miami tritium sample results was incomplete.

#### **Table 4.2-9 Background Perchlorate Concentration in the Pajarito Plateau Groundwaters (NMED 2004, 88768)**



<sup>a</sup> The mean is calculated as the arithmetic average

 $<sup>b</sup>$  Std. Dev. = standard deviation</sup>

 $\textdegree$  CV = coefficient of variation = Std. Dev /Mean

 $TDS$ **CACO3/L) Ba Ca Co3/L) Ba CO3/L) Ba CO3/L) Ba CO3/L) Ba CO4/L) Ba CO4/L) Da CO4/L, Da CO4/L,** 178  $113$ **Water Canyon Gallery** 0.012 41.1 0.009 7.04 0.91 0.07 0.03 1.58 3.13 [0.001] 5.6 [0.02] 0.36 [0.02] 1.14 0.049 113  $134$ Upper Cañon de Valle | 0.042 | 0.042 | 0.028 | 0.24 | 0.07 | 0.07 | 0.26 | 0.31 | 0.026 | 0.35 0.088 | 0.35 | 0.36 | 0.36 | 0.36 | 1342 | 0.088 | 1342 | 0.088 | 14.9 | 14.942 | 0.088 | 13.39 | 0.036 | 0.036 | 0.042 | 0.042 **Pine** 0.12 64.2 0.059 18.3 2.98 0.10 0.16 5.55 4.15 0.32 6.4 0.12 0.27 0.33 16.5 0.12 181 **Apache** 0.045 55.0 0.072 13.2 16.9 0.05 0.08 4.56 5.02 0.009 10.4 [0.02] 0.26 0.03 5.26 0.11 178  $181$ 0.049 0.088  $0.11$  $0.12$ ທັ SO<sub>4</sub> 3.36 16.5 5.26  $1.14$ **Analytical Results (ppm) for Selected Springs within the Sierra de los Valles (June 2000)**  Analytical Results (ppm) for Selected Springs within the Sierra de los Valles (June 2000) PO<sub>4</sub>(P)  $[0.02]$  $0.14$ 0.03 0.33  $NO_3(N)$ 0.36 0.35 0.26 0.27  $\vec{E}$  $[0.02]$  $[0.02]$ 0.03  $0.12$  $10.4$  $\tilde{\mathbf{z}}$ 5.6  $6.4$  $4.9$  $[0.001]$ 600'0 0.015 έ 0.32 5.02  $3.31$ 4.15  $3.13$ ξ 2.86 5.55 1.58  $0.08$  4.56  $\check{\phantom{1}}$ 0.16 0.03 0.07 டீ 0.05 0.06  $0.10$ 0.07 ц. 16.9  $0.91$ 1.24 2.98  $\overline{\mathbf{o}}$  $13.2$ 7.04  $12.2$ 18.3 යී  $0.028$ 0.059 0.072 0.009 Bã **(mg Alkalinity**  51.6 64.2 55.0  $41.1$ 0.045 0.012 0.042  $0.12$  $\bar{\mathbf{z}}$ **Spring Al**  Upper Cañon de Valle **Water Canyon Gallery** Spring Apache Pine

**Table 4.4-1** 

**Table 4.4-1** 

Note: Concentrations of total dissolved solids (TDS) were calculated from the summation of solutes. [0,001] means less than detection with the method detection limit given in<br>brackets Note: Concentrations of total dissolved solids (TDS) were calculated from the summation of solutes. [0.001] means less than detection with the method detection limit given in brackets.

## **Appendix A**

*Samples Taken and Field Measurements* 

## **Appendix B**

*Statistical Plots and Tables* 

### **Figures**



#### **Tables**

#### **Location by Metals**



### **Location by Other Analytes**



#### **Location by Radionuclides**





**Figure B-1. Time sequence of aluminum, antimony, and arsenic results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-2. Time sequence of barium, beryllium, and boron results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-3. Time sequence of cadmium, calcium, and chromium results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-4. Time sequence of cobalt, copper, and iron results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-5. Time sequence of lead, magnesium, and manganese results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-6. Time sequence of mercury, molybdenum, and nickel results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-7. Time sequence of potassium, selenium, and silver results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-8. Time sequence of sodium, strontium, and thallium results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-9. Time sequence of uranium and zinc results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-10. Time sequence of alkalinity, ammonium, and bicarbonate results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-11. Time sequence of dissolved organic carbon, chloride, and fluoride results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-12. Time sequence of nitrate, nitrite, and silicon results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-13. Time sequence of total dissolved solids, deuterium/hydrogen ratio, and delta deuterium vs std. mean ocean water results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-14. Time sequence of nitrogen-15/nitrogen-14 ratio and oxygen-18/oxygen-16 ratio results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-15. Time sequence of gross alpha radiation, americium-241, and plutonium-238 results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-16. Time sequence of plutonium-239/240, uranium-234, and uranium-235 results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 



**Figure B-17. Time sequence of uranium-238, strontium-90, and tritium results [note that "x" indicates detected concentrations, and "o" indicates nondetect results/2]** 

# **Appendix C**

*Statistical Plots* 

## **Figures**






## **Figure C-1. Temperature plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]**



## **Figure C-2. Specific conductance (conductivity) lots [note that "+" signs are nonfiltered samples and that squares are filtered samples]**



**Figure C-3. pH plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-4. Aluminum plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-5. Antimony plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-6. Arsenic plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 







**Figure C-8. Beryllium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-9. Boron plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-10. Cadmium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-11. Calcium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-12. Total chromium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-13. Cobalt plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-14. Copper plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-15. Iron plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-16. Lead plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-17. Magnesium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-18. Manganese plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-19. Mercury plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-20. Molybdenum plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-21. Nickel plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-22. Potassium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-23. Selenium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-24. Silver plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-25. Sodium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-26. Strontium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-27. Thallium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-28. Uranium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-29. Zinc plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-30. Alkalinity plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-31. Ammonium plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 







**Figure C-33. Dissolved organic carbon plots [note squares are filtered samples]** 



**Figure C-34. Chloride plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-35. Fluoride plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-36. Nitrate [reported as N] plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]**


**Figure C-37. Nitrite [reported as N] plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-38. Silica plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-39. Total dissolved solids and total solids plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-40. Deuterium/hydrogen ratio plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-41. Delta deuterium versus standard mean oceanic water plots [note "+" are nonfiltered samples]** 



**Figure C-42. Nitrogen-15/nitrogen-14 ratio plots [note "+" are nonfiltered samples]** 



**Figure C-43. Oxygen-18/oxygen-16 ratio plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-44. Gross alpha radiation plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-45. Americium-241 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-46. Plutonium-238 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-47. Plutonium-239,240 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-48. Uranium-234 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-49. Uranium-235 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-50. Uranium-238 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-51. Strontium-90 plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 



**Figure C-52. Tritium ALL [combined analytical laboratory data] plots [note that "+" signs are nonfiltered samples and that squares are filtered samples]** 

# **Appendix D**

*Statistical Analyses of Pre-1997 Hydrogeochemical Data* 

# **Figures**



#### **Tables**



# **D.1 STATISTICAL ANALYSES OF PRE-1997 HYDROGEOCHEMICAL DATA**

This section presents results of statistical analyses performed on pre-1997 groundwater-quality data collected within and surrounding the Laboratory. This statistical analysis was performed as a basis of comparison to the data collected in 1997 and later years. Sources of groundwater-quality data are defined, and the accuracy and precision of the data are evaluated. Analytical precision for nonfiltered water samples is usually poor because of the presence of suspended solids, which when partially or completely digested with nitric acid at pH 2 or less introduce false positives for metals and trace elements. Therefore, groundwater data were screened to evaluate analytical results mainly for those samples that were filtered before analyses.

# **D.1.1 Methodology**

# **D.1.1-1 Data Adequacy of Water Samples**

Data adequacy of the pre-1997 groundwater background data was evaluated by both qualitative and quantitative methods. Analytical results for filtered groundwater samples from different data sources were evaluated. Removal of suspended solids in filtered samples was essential to evaluate baseline or background hydrochemistry. The presence of suspended solids positively biases concentrations of analytes because of partial or complete dissolution of the solids during acidification of the water samples. Digestion of suspended solids in water samples also results in poor charge balances ( $> \pm 10\%$ ), and the charge balance relationship is one quantitative metric of data quality.

The overall adequacy of the data was assessed by evaluating the standardized residuals from the regression analysis of total dissolved anions versus total dissolved cations. One metric is based on the frequency of standardized residuals with an absolute value greater than 1.96. The expected value of residuals with this magnitude is 5%, and the data set would be judged to be in charge balance if the frequency of residuals is not statistically different from 5%.

Charge-balance errors for the pre-1997 analytical results were calculated for major and trace ions as follows:

(100)[( $\Sigma$  milliequivalents cations –  $\Sigma$  milliequivalents anions) divided by  $(\Sigma$  milliequivalents cations +  $\Sigma$  milliequivalents anions)]

Other quantitative metrics of data quality employed the calculation of variability resulting from replicate laboratory analyses of the same sample. This value provided a baseline for temporal variation in samples collected from a given location, as well as differences in concentration between sampling locations.

# **D.1.1-2 Exploratory Data Analyses**

Statistical analyses of the selected pre-1997 background data involve several exploratory data analysis (EDA) tools. The purpose of EDA is to identify possible outliers in the data, understand relationships between analytes, evaluate parametric and nonparametric statistical modeling options, and determine the frequency of nondetect values by analyte and by potential data subpopulations.

One of these methods involves bivariate plots. A bivariate plot of anion sum versus cation sum is shown in Figure D.1-1. A bivariate plot of laboratory duplicates (mean values) versus relative standard deviation is shown in Figure D.1-2. A correlation matrix for major ions, cation sum, and anion sum is provided in Figure D.1-3. Figure D.1-4 consists of total dissolved solids (TDS) versus bicarbonate concentrations for

different aquifer material made up of alluvial and perched intermediate groundwater and the regional aquifer.

The first step for EDA is the assembly of the data set under evaluation, which includes a summary of the number of samples collected from each location (Table D.1-1). Other tools include normal quantile plots of untransformed and transformed data (Figure D.1-5), box plots to compare possible data groups (Figure D.1-6), and statistical data summaries (Tables D.1-2 and D.1-3). Based on these sample data, the concentration range of nondetect and detect data can be summarized.

Box plots: Box plots are used to show differences between two or more sample collection areas, or depths. This type of plot is shown as Figures D.1-5 and D.1-6. Box plots summarize information about the shape and spread of the distribution of concentrations for an analyte. They consist of a box and a (median) line across the box. The y-axis shows the observed concentrations in the reported units. The area enclosed by the box shows the concentration range containing the middle half of the data; that is, the lower box edge is at the 25th percentile, and the upper box edge is at the 75th percentile. The height of the box is a measure of the spread of the concentrations. The horizontal line across the box represents the median (50th percentile) of the data, which is a measure of the center of the concentration distribution. If the median line divides the box into two approximately equal parts, the shape of the distribution of concentrations is symmetric; if not, the distribution is skewed or nonsymmetrical. All concentrations are plotted as points overlying the box plot.

Normal quantile plots: As a companion plot to some box plots, the normal quantile plots for the data groups are also depicted in Figures D.1-5 and D.1-6. Normal quantile plots (also known as a normal quantile-quantile or q-q plot) are a particular type of quantile plot. The data set concentrations are plotted in increasing order and spread out to allow for comparison of their distribution to that of a theoretical distribution, the standard normal distribution. The quantiles of the data set (y-axis) are plotted against the quantiles for a standard normal (x-axis). The quantiles of a standard normal, that is normal with mean  $= 0$ and standard deviation = 1, are those for the theoretical distribution and can be found in published tables of the cumulative normal distribution. For example, the 50th quantile is 0, the 90th quantile is approximately 1.282, the 95th quantile is about 1.645, etc. If data are derived from a normal statistical distribution, the points in the plot will lie close to the diagonal straight line overlying the data points. The subsets of the data set that differ the most from those expected from a normal distribution are seen as points straying from the line. Multiple data groups can be compared to each other and to a normal distribution by plotting a separate line for each data set in the same display. The observer can see where, if anywhere, the two plots follow the same line, overlap or intersect, indicating that they have equal concentrations at that (those) associated quantile(s).

Regression analysis and scatter plots: Regression analysis provides a measure of the association between pairs of variables. An *x-y* scatter plot is used to graphically depict this relationship. Regression analysis provides a correlation coefficient and an associated measure of statistical significance (or p-value). The correlation coefficients can potentially range between –1 and +1. A correlation coefficient of zero indicates no correlation between the two measurements. A correlation coefficient of +1 indicates a perfect positive relationship between the measurements. A correlation coefficient of –1 indicates a perfect negative relationship (no correlation) between the measurements.

# **D.2 STATISTICAL AND GEOCHEMICAL ANALYSES OF PRE-1997 WATER-QUALITY DATA SETS**

#### **D.2.1 Data Evaluation**

Table D.1-1 presents a summary of the analytes included in the available background hydrogeochemical data and the range of nondetect and detected values. The pre-1997 data were derived from seven data sources and were collected at irregular intervals from June 1978 to July 1996.Most of the major elements were always detected, but many of the trace elements have low detection rates. A low detection rate limits the utility of many statistical analyses. Varying analytical methods greatly influence analytical method detection limits (MDLs) for the analytes. Chemical results for water samples reported by the Laboratory's Earth and Environmental Sciences group, EES-6, Shevenell et al. (1987, 06673), Vuataz and Goff (1986, 73686), Dale et al. (1996, 57014), and Yanicak (1998, 57583) were analyzed by either AA (metals), ICPOES (metals), IC (anions), and/or inductively coupled plasma mass spectrometry (ICPMS) (metals). Water samples collected under the National Uranium Resource Evaluation (NURE) Project were analyzed by neutron activation analysis (NAA) and delayed neutron activation analysis (DNAA). Analytical results for nitrogen species were reported as nitrogen compounds (nitrate and nitrite) and not as nitrogen. The same reporting procedure applies to phosphorus (phosphate).

The analysis of the charge balance for 55 water samples showed good agreement between the cation sum and the anion sum (Figure D.1-1 and Table D.2-2). In five values out of 55, the absolute value of the standardized residual exceeded 1.96, (mean plus  $2 \sigma$ ) which represents 9% rather than the expected 5%. This outcome is not improbable under the assumption that the statistical problem represents a binomial experiment of 55 trials with a probability of success of 5% per trial.

There were 10 laboratory duplicates for the groundwater samples. Because many of the trace element (e.g., beryllium, antimony, cadmium) results were nondetects, the agreement between the laboratory duplicates could not be calculated for many analytes. Figure D.1-2a and 2b show the laboratory duplicate variation as a function of the mean concentration of the laboratory duplicate results. The data show, excluding sample AAB1336 (Figure D.1-2b), that with the exception of two values with mean analyte concentrations near zero, laboratory variation is less than a 20% relative standard deviation.

The interrelationship of five major solutes (silica, calcium, sodium, bicarbonate, and chloride) with TDS, anion sum, and cation sum are shown in Figure D.1-3. This correlation matrix suggests significant correlations between sodium, bicarbonate, TDS, and anion and cation sums. This correlation implies that there are geochemical interactions between sodium and bicarbonate and that these two solutes contribute to TDS and cation/anion sums. These geochemical distinctions were used to separate different aquifers (e.g., alluvial, intermediate, and regional). For example, La Mesita spring is a sodiumbicarbonate-type water. However, silica correlates poorly with sodium and bicarbonate and this demonstrates that silica does not form complexes with sodium and bicarbonate in this groundwater. The correlation matrix also shows an apparent outlier value for calcium.

A more detailed correlation plot shows the relationship between bicarbonate and TDS (Figure D.1-4). This plot shows that groundwater samples collected from the Santa Fe Group (regional aquifer) have the highest concentrations of both bicarbonate and TDS and exhibit the greatest variation.

To evaluate the appropriate parametric distribution for statistically modeling the groundwater background data, two types of graphical displays are used to interpret the data. Figure D.1-5 shows histograms and probability plots for bicarbonate and TDS for all data combined over aquifers. Bicarbonate was selected because it is the dominant anion contributing to TDS. Figure D.1-6 shows box plots and probability plots by aquifer group for bicarbonate and TDS. These plots suggest that the combined data represent a

mixture distribution based on differences in aqueous geochemistry between aquifers, where the major difference is between the Santa Fe Group/Puye Formation versus the alluvial/Bandelier Tuff/Cerros del Rio basalt/Tschicoma Formation.

# **D.3 CONCLUSIONS**

Adequacy of the pre-1997 groundwater baseline data was evaluated by both qualitative and quantitative methods. Analytical results for filtered groundwater samples from different data sources were evaluated. The removal of suspended solids by filtration of samples was essential for evaluating background hydrochemistry.

The analysis of the charge balance for 55 water samples showed good agreement between the cation sum and the anion sum. There were five values out of 55 where the absolute value of the standardized residual exceeded 1.96, which represents 9% rather than the expected 5%.

There were ten laboratory duplicates for the 55 groundwater samples. Because many of the results were nondetect, the agreement between the laboratory duplicates could not be calculated for many analytes.

The interrelationships of five major solutes (silica, calcium, sodium, bicarbonate, and chloride) with TDS, anion sum, and cation sum were evaluated. This correlation matrix suggests significant correlations between sodium, bicarbonate, TDS, and anion and cation sums.

Groundwater samples collected from the Santa Fe Group (regional aquifer) have the highest concentrations of bicarbonate and TDS. The regional aquifer also shows the greatest variation in TDS and individual solutes.

To evaluate the appropriate parametric distribution to statistically model the groundwater background data, two types of graphical displays are used to interpret the data. Histograms and probability plots for bicarbonate and TDS for all data were combined for the three aquifer types: alluvial, volcanic (perched intermediate), and the regional aquifer. Box plots and probability plots by aquifer group for bicarbonate and TDS suggest that the combined data represent a mixture distribution based on differences in aqueous geochemistry between aquifers. The major difference is between the Santa Fe Group/Puye Formation versus the alluvial/Bandelier Tuff/Cerros del Rio basalt/Tschicoma Formation.



**Figure D.1-1. Evaluation of charge balance for background water samples (filtered) (cation sum = 0.04429 + 1.00292 anion sum, r2 = 0.982, n = 55 samples)** 



**Figure D.1-2. Summary of variability from laboratory duplicate analyses. (a) Samples AAB1336, AAB8498, AAB8512, and 0441-95-0013. (b) Samples AAB8498, AAB8512, and 0441- 95-0013. Excluding sample AAB1336 in plot (b) results in a laboratory variation of less than 20% of the relative standard deviation, with the exception of two samples with mean analyte concentrations near zero. See Figure D.1-1 for symbols representing sample sites.** 



**Figure D.1-3. Correlation matrix of major solutes, anion sum, and cation sum. See Figure D.1-1 for symbols representing sample sites.** 



**Figure D.1-4. Relationship between TDS and bicarbonate for pre-1997 baseline groundwater samples. See Figure D.1-1 for symbols representing sample sites.** 



Figure D.1-5. Histogram and normal probability plots for a) bicarbonate (HCO<sub>3</sub>) and b) TDS for **pre-1997 baseline groundwater samples (filtered). See text for statistical nomenclature and Figure D.1-1 for symbols representing sample sites.** 



**Figure D.1-6. Box plots showing a) bicarbonate and b) TDS by aquifer material for pre-1997 baseline groundwater samples. See text for statistical nomenclature and Figure D.1-1 for symbols representing sample sites.** 



					Data Sources				
		Blake et al (1995,	EES-6	<b>ER</b> Project	Meeker et al.	57014); Yanicak Dale et al. (1996	Shevenell et al.		
Group	Location	49931)	$(1994 - 1995)$	$(1994 - 1995)$	(1990, 54783)	(1998, 57583)	(1987, 06673)	NURE	Total
(1) Alluvial	LAO-B	$\circ$	4	7(3)	$\circ$	$\circ$	$\circ$	$\circ$	11(3)
	Pine Spring			$\circ$	0	Ю	0		ထ
(2) Volcanic rocks	Apache Spring	ᡪ	$\sim$	$\circ$	0	0	ᡪ	0	4
	LAOI(A)-1.1	0	ω	$\frac{4}{4}$	0	$\circ$	0	0	4 (4)
	Seven Springs	᠇	$\overline{\phantom{0}}$	0	ᡪ	$\circ$	Ω	$\overline{\phantom{0}}$	r
	Upper Cañon de Valle	$\circ$	$\circ$	$\circ$	0	᠇	0	0	
	Water Canyon Gallery	Z	ᡪ	$\circ$	$\circ$	$\circ$	$\overline{\phantom{0}}$	$\circ$	4
(3) Regional aquifer	Doe Spring	$\overline{\phantom{0}}$	5	$\circ$	$\circ$	$\sim$	0	$\circ$	$\infty$
	Guaje Canyon Well #5	$\mathbf{\sim}$	$\circ$	0	0	0	0	0	2
	Otowi #4	Ν	$\circ$	$\circ$	0	0	0	0	$\mathbf{\mathsf{N}}$
	Pajarito Spring	$\mathbf{\sim}$	4	0	0	$\sim$	$\overline{\phantom{0}}$	0	თ
	Sacred Spring	$\overline{\phantom{0}}$		0	0	0	$\overline{\phantom{0}}$	0	ω
	Spring 1	$\circ$	$\mathbf{\Omega}$	$\circ$	0	ო	0	0	ю
	Spring 9B	0		$\circ$	0	ᡪ	$\circ$	$\circ$	$\mathbf{\tilde{z}}$
Total		\$	25	8 (7)		4	r	$\mathbf{\Omega}$	70 (7)

Note: Values in parentheses represent laboratory duplicate results.<br>NURE = National uranium resource evaluation. Note: Values in parentheses represent laboratory duplicate results. NURE = National uranium resource evaluation.

		Nondetects			<b>Detects</b>		Detection
Analyte	Count	Min	Max	Count	Min	Max	Rate
Anion Sum	0	$n/a^*$	n/a	46	0.832	2.85	100%
Balance	$\overline{4}$	0.0026	0.012	34	0.0046	0.2757	89%
<b>Cation Sum</b>	0	n/a	n/a	46	0.865	3.298	100%
<b>DOC</b>	0	n/a	n/a	3	2.4	5.8	100%
TDS	0	n/a	n/a	58	102.4	308.2	100%
В	30	0.003	0.1	38	0.003	0.73	56%
Br	22	0.00001	0.001	23	0.00001	0.00027	51%
Сa	0	0	$\pmb{0}$	72	1.63	67	100%
СI	10	0.001	0.005	55	0.00064	0.00985	85%
CO <sub>3</sub>	43	0	0.005	4	0.0059	0.008	9%
F	10	0.00001	0.0005	57	0.00003	0.00098	85%
HCO <sub>3</sub>	0	0	0	58	0.0335	0.137	100%
Κ	$\overline{2}$	2.2	2.6	68	1.4	21	97%
Li	22	0.004	0.02	40	0.005	0.08	65%
Mg	3	$\mathbf{1}$	3.08	69	0.29	16	96%
Na	0	0	0	70	4.9	58	100%
SiO <sub>2</sub>	0	0	0	68	0.014	0.105	100%
SO <sub>4</sub>	$\overline{7}$	$\mathbf{1}$	50	60	1.05	66	90%
Sr	$\overline{c}$	0.1	0.1	66	0.02	3.5	97%
Ag	66	0.0002	0.1	$\mathbf{1}$	0.014	0.014	1%
Al	16	0.1	0.2	42	0.03	2.71	72%
As	37	0.0002	0.1	23	0.0002	0.013	38%
Ba	19	0.01	0.12	50	0.01	0.35	72%
Be	34	0.001	0.1	$\overline{\mathbf{c}}$	0.009	0.01	6%
Cd	63	0	0.03	6	0.001	0.03	9%
Co	65	0	0.06	4	0.003	0.081	6%
Cr	40	0	0.03	29	0.001	0.066	42%
Сs	35	0	0.01	4	0.002	0.008	10%
Cu	36	0	0.04	33	0.002	0.06	48%
Fe	27	0.01	0.1	44	0.01	4.17	62%
Hg	51	0.0002	0.2	5	0.0004	0.2	9%
L	38	0	0	0	0	0	0%
Mn	54	0.002	0.05	15	0.001	$8.8\,$	22%

**Table D.2-1 Summary of pre-1997 Groundwater Data for Background Locations (Concentration Units in mg/L or ppm)** 





\*n/a = Not applicable.

# **Table D-2.2 Summary of pre-1977 Samples Where Anions Do Not Balance Cations**



# **Appendix E**

*Descriptions of Wells and Springs*
# **Figures**



# **E.1 APACHE SPRING (LAVA IN TSCHICOMA FORMATION)**

**Location:** Bland 7.5 min USGS topo quad (Latitude N 35˚49'28.3", Longitude W106˚23'23.36709", Elevation 2522 m)

**Ownership: Bandelier National Monument** 

**Geologic Map:** Smith et al. (1970, 09752); Goff et al. (1990, 21574)

**Description:** Apache Spring issues on the north side of a shallow ravine about 0.5 km south of State Highway 4 in the southern Sierra del los Valles. The spring orifice is covered by a rock and concrete crib from which water leaks out at the base (Figure E.1-1). The maximum recorded flow is 15 L/min, but on most occasions it is much less. The groundwater is not used for human consumption or irrigation.

The spring discharges from colluvium consisting of angular blocks of gray, densely welded rhyolite tuff (Tshirege Member, Bandelier Tuff) and gray porphyritic dacite (Tschicoma Formation, Polvadera Group) in a matrix of volcanic sand and soil. About 10 m above the spring, outcrops of dacite with pronounced horizontal platy jointing are exposed along the access trail (Figure E.1-2). The dacite contains phenocrysts of plagioclase, hornblende, orthopyroxene, and clinopyroxene in a sugary, devitrified matrix. The contact of dacite with overlying ignimbrite is hidden, but its approximate location can be identified using the presence of float, about 20 m above the spring.

#### **E.2 SPRING 9B (LAVA AND HYDROMAGMATIC DEPOSITS IN CERROS DEL RIO VOLCANIC FIELD)**

**Location:** White Rock 7.5 min USGS topo quad (Latitude N35˚45'40.46", Longitude W106˚14'36.88", Elevation 1674 m)

#### **Ownership:** U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752); Dethier (1997, 49843)

**Description:** Spring 9B issues from a small cave eroded into the intersection of a cooling joint and basal scoria at the bottom of a lava flow (Figure E.2-1). The spring occurs on the northwest side of White Rock Canyon, roughly 200 m downstream of the mouth of Chaquehui Canyon. The spring is about 25 m above the Rio Grande. The flow rate is ≤3 L/min. The spring water supports the growth of a wedge of trees and shrubs that fill a shallow ravine descending towards the river (Figure E.2-2).

The geology of White Rock Canyon at this location has been described by Heiken et al. (1996, 54425, Figure W18). From bottom to top, the stratigraphy consists of hydromagmatic (maar) deposits, a sequence of interbedded basalt flows and hydromagmatic deposits, a thick lava flow of benmoreite (a type of chemically evolved basalt), and the Tshirege Member of the Bandelier Tuff (Figure E.2-2). The mafic deposits beneath the tuff are part of the Cerros del Rio volcanic field.

The lava flow hosting Spring 9B is the lowest exposed lava in this sector of the canyon wall and is a tholeiite dated at 2.78 ±0.04 Ma. The benmoreite is dated at 2.75 ±0.08 Ma (WoldeGabriel et al. 1996, 54427) and is an important stratigraphic marker. It consists of at least two flow units of highly foliated lava, locally exceeds 100 m in thickness, and extends into Frijoles Canyon. It is the highest lava flow in the sequence at Upper Falls in Frijoles Canyon. The dates indicate that roughly 215 m of Cerros del Rio deposits were emplaced in <100 ka.

The hydromagmatic beds beneath Spring 9B display classic characteristics of such deposits (Fisher and Schminke 1984, 88744; Heiken et al. 1996, 54425; Figure. E.2-3). They consist of massive to crossbedded sandstone, siltstone, and mudstone composed of basalt and basaltic glass with subordinate quartz, microcline, and crystalline rock grains. The basaltic glass has been altered to a pale-brown-toyellow palagonite clay. Accretionary lapilli up to 0.5 cm in diameter are found in some of the muddy layers. Basalt bomb sags deform the beds, particularly the mudstone layers. Lithic fragments consist of angular basalt and rounded-to-subrounded cobbles and pebbles of quartzite, microcline, granite, gneiss, and intermediate-composition volcanic rocks. Occasional coarse-grained lenses of the latter rocks are scattered throughout the beds. These lithologies originate from beds in the Santa Fe Group underlying Cerros del Rio deposits.

# **E.3 DOE SPRING (HYDROMAGMATIC DEPOSITS IN THE CERROS DEL RIO VOLCANIC FIELD)**

**Location:** White Rock 7.5 min USGS topo quad (Latitude N35˚45'53.51", Longitude W106˚14'34.55", Elevation 1689 m)

**Ownership:** U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752); Dethier (1997, 49843)

**Description:** Doe Spring flows from the northeast wall of lower Chaquehui Canyon, about 30 m above the canyon floor. The spring drips from several discharge points, forming a wet, moss-covered wall (Figure E.3-1) and has a total discharge of ≤5 L/min. Individual sampling points have considerably less flow. The spring is partially hidden by heavy brush and vegetation and is accessed from a short path that climbs up the canyon wall. The spring water is used by game and is not considered potable for humans.

The spring issues from fractures in bedded, hydromagmatic (maar) deposits underlying a lava flow dated at 2.78 Ma (WoldeGabriel et al. 1996, 54227; see description of Spring 9B above). Additional lava flows dated as young as 2.45 ±0.06 Ma occur higher in the northern wall of Chaquehui Canyon (WoldeGabriel et al. 1996, 54227). The maar deposits display cross-bedding, and contain basalt bombs, sag structures, abundant cobbles, and lithic fragments of quartzite and microcline. Pale-brown-to-yellow palagonitic alteration of basaltic glass is evident. These deposits and lavas are part of the Cerros del Rio volcanic field. Careful inspection of Chaquehui Canyon revealed no exposures of sedimentary deposits of the Santa Fe Group as implied by Purtymun (1995, 45344).

#### **E.4 LA MESITA SPRING (LANDSLIDE? IN SANTA FE GROUP)**

**Location:** White Rock 7.5 min USGS topo quad (Latitude N35˚52'13.74", Longitude W106˚08'34.23", Elevation 1701 m)

**Ownership:** San Ildefonso Pueblo

**Geologic Map:** Smith et al. (1970, 09752); Dethier (1997, 49843)

**Description:** La Mesita Spring issues within a shallow ravine on the northwest side of Buckman Mesa (La Mesita) about 500 m downstream of the Otowi Bridge that spans the Rio Grande. The ravine is filled with trees and shrubs (Figure E.4-1) watered by the spring. The uppermost source of water is about 20 m above river level, and the flow rate is ≤5 L/min (Figure E.4-2). The spring water is used by livestock and game and is not considered potable for humans.

Dethier (1997, 49843) indicates that all rocks in this area consist of coalesced landslides. Older rocks consist of unconsolidated sedimentary deposits of the Santa Fe Group having a consistent but shallow dip to the east. Along ridge crests, these older sediments are covered with coarse-grained gravels of the ancestral Rio Grande. Draperies of these gravels and basalt blocks and scoria from La Mesita cover the slopes. The basalt blocks are derived from the Cerros del Rio volcanic field.

# **E.5 PAJARITO SPRING (4A)(LANDSLIDE BLOCK IN CERROS DEL RIO VOLCANIC FIELD, TOTAVI LENTIL, AND SANTA FE GROUP)**

**Location:** White Rock 7.5 min USGS topo quad (Latitude N35˚56'34.4", Longitude W106˚11'47.38", Elevation 1703 m)

**Ownership:** Los Alamos County

**Geologic Map:** Smith et al. (1970, 09752); Dethier (1997, 49843)

**Description:** Pajarito Spring (Spring 4A of Purtymun 1995, 45344) issues from near the base of an eastfacing landslide (toreva) block in White Rock Canyon about 0.4 km west of the Rio Grande. There are actually several discharge points for the spring, which collect to form a small creek flowing south in a ravine between two large landslide blocks. The total flow rate of the spring(s) usually exceeds 300 L/min. The largest spring source, which we sampled from, occurs in a stand of trees and shrubs (Figure E.5-1).

Rocks in the discharge channel of the spring consist primarily of angular basalt (Cerros del Rio volcanic field) and minor rounded cobbles of quartzite, chert, and other lithologies. Exposures of the toreva block from which the spring issues are found in a gully about 70 m south of the spring. Rocks in the lower gully wall consist of large jumbled boulders of basalt in a pink-to-tan matrix of arkosic-to-volcanic sand. Occasional blocks of bedded siltstone and mudstone up to 1 m long are also incorporated into the jumble (Figure E.5-2). Parts of the matrix and fragments resemble lithologies in the Santa Fe Group. Because of slumping, cracks and small open spaces form around fragment margins in the toreva block.

Higher up on the gully wall, the basalt boulders are interbedded with layers containing rounded cobbles and pebbles of river gravel in a sandy matrix (Figure E.5-3). The cobbles consist primarily of quartzite, other crystalline rocks (granite and gneiss), altered intermediate-to-silicic composition volcanic rocks, chert, and basalt such as those that occur in the Totavi Lentil.

The large landslide block east of the ravine consists of about 25 to 30 m of interbedded gravel, sandstone, and siltstone overlain by about 20 m of jumbled basalt blocks. A lag of coarse river gravel occurs on the south shoulder of the landslide block. The cobbles in the gravels resemble those in the Totavi Lentil. Small patches of unconsolidated El Cajete Pumice are found in flat areas on top of the landslide complex both above and below the spring area.

# **E.6 PINE SPRING (PUYE FORMATION AND LAVAS OF THE KERES GROUP)**

**Location:** Guaje Mountain 7.5 min USGS topo quad (Latitude N35˚57'21.95", Longitude W106˚17'04.52", Elevation 2206 m)

**Ownership:** U.S. Forest Service

**Geologic Map:** Smith et al. (1970, 09752), Kempter and Kelley (2002, 88777)

**Description:** Pine Spring is located in upper Garcia Canyon on the east side of Forest Service Road 445 at Bench Mark 7216, about 6 km north of Los Alamos. The foundation of a burned log cabin stands in a small clearing on a rise west of the road. The spring is surrounded by a circular crib of cemented stone, which is breached on the south side and from which grows a ponderosa pine tree (Figure E.6-1). The

water is generally murky, and the flow rate rarely exceeds 2 L/min. Other springs occur in the gullies 0.2 to 0.5 km west of the road. The springs are used by livestock and game but are not considered potable for humans.

Pine Spring lies on the down-thrown side of a north-south-trending fault juxtaposing alluvium consisting of boulder-bearing sediments of the Puye Formation (to the west) against mafic-to-intermediate composition lavas and overlying Puye deposits (to the east) (Smith et al. 1970, 09752; Kempter and Kelley 2002, 88777). The Tshirege Member of the Bandelier Tuff covers the mesa tops. Poorly exposed fall deposits of the Cerro Toledo Rhyolite occur between the Puye sediments and the Bandelier Tuff in a gully on the bluff east of the spring.

The lowermost lava in the bluff east of the fault is exposed about 150 m downstream of the spring (Figure E.6-2). It is highly fractured and weathered, and appears to be an olivine andesite. It contains rare phenocrysts of plagioclase and microphenocrysts of iddingsite-bearing olivine in a sugary groundmass of plagioclase, orthopyroxene, and clinopyroxene. Smith et al. (1970, 09752) assigned the andesite to the Lobato Basalt.

# **E.7 SACRED SPRING (SANTA FE GROUP)**

**Location:** Puye 7.5 min USGS topo quad (Latitude N35˚53'33.05" Longitude W106˚08'59.13", Elevation 1722 m)

**Ownership:** San Ildefonso Pueblo

**Geologic Map:** Smith et al. (1970, 09752)

**Description:** Sacred Spring is a pool about 10 m in diameter that occurs in a small, grassy clearing surrounded by cottonwood trees **(**Figure E.7-1). The spring is located south of a shallow ravine about 0.5 km north of the junction of State Highways 4 and 30 and about 100 m east of State Highway 30. The spring flow is usually diffuse, and the flow rate rarely exceeds 5 L/min. The spring is used mostly by livestock and game and is not considered potable for humans.

Sacred Spring issues from unconsolidated, pale-pink-to-tan sedimentary rocks of the Santa Fe Group. Nearby terraces are overlain by coarse-grained gravels of the ancestral Rio Grande. Bluffs located about 0.5 km west of the spring expose gray beds of the Puye Formation (Figure E.7-2) overlying the Santa Fe Group. The extrapolated contact between the Santa Fe Group and the Puye Formation is roughly 10 to 20 m above the position of the spring.

#### **E.8 SEVEN SPRINGS (OTOWI MEMBER, BANDELIER TUFF)**

**Location:** Seven Springs 7.5 minute USGS topo quad (Latitude N35˚48'14.05", Longitude W106˚42'14.0", Elevation 2482 m)

**Ownership:** U.S. Forest Service

**Geologic Map:** Smith et al. (1970, 09752)

**Description:** Seven Springs discharges from the west side of a narrow valley in Calaveras Canyon, about 400 m upstream of State Highway 126, west of the Valles Caldera on the Jemez Plateau. There are several springs in the immediate vicinity, some discharging from valley alluvium, some from outcrops of densely welded rhyolite tuff. University of New Mexico researchers (C. Dahm, L. Crossey, and M. Campana) have been conducting long-term hydrologic and geochemical measurements in the vicinity.

Water from the springs is collected into a 10-in.-diameter pipeline that heads downstream towards the Fish Hatchery on the Rio Cebolla and the small community of Seven Springs.

The Laboratory took samples from the largest spring, which issues from an open crack in a low cliff of welded tuff about 2 m above the valley floor (Figure E.8-1). Flow rates over the past 20 years have varied considerably. On some occasions, spring water literally forms a 1-m-high fountain or "rooster tail" at the crack. Shevenell et al. (1987, 06673) report a flow rate of 60 L/min. During dry periods, the flow is much less. Immediately below the spring, the water flows through a small pool filled with watercress.

The tuff, which is the Otowi Member of the Bandelier Tuff, is quite different in appearance at Seven Springs than on the Pajarito Plateau east of Valles Caldera. At Seven Springs it is a gray, densely welded, lithic rich, and devitrified ignimbrite, with pale gray fiamme. The tuff has a pronounced horizontal foliation and erodes into hackly plates about 3 to 10 cm wide. Phenocrysts consist of clear quartz, clear sanidine, and tiny dark-green-to-black clinopyroxene. Lithic fragments consist primarily of black andesitic rocks.

The Otowi Member forms a steep slope that rises about 50 m to a cliff formed of the Tshirege Member of the Bandelier Tuff (Smith et al. 1970, 09752). There is no Tsankawi pumice fall deposit at the contact immediately above the springs. Rather, the contact is undulating, suggesting that there was too much relief for fall deposits to remain in place. The basal part of the Tshirege is composed of nonwelded tuff with occasional large pumice fragments (≤20 cm). Lithic fragments consist primarily of black andesitic rocks.

# **E.9 SPRING 1 (LANDSLIDE BLOCK IN CERROS DEL RIO VOLCANIC FIELD, TOTAVI LENTIL, AND SANTA FE GROUP)**

**Location:** White Rock 7.5 min USGS topo quad (Latitude N35˚51'32.55", Longitude W106˚08'34.08", Elevation 1702 m)

#### **Ownership:** San Ildefonso Pueblo

**Geologic Map:** Smith et al. (1970, 09752), Dethier (1997, 49843)

**Description:** Spring 1 issues from a small bench covered with trees and vegetation about 40 m above the northeast side of the Rio Grande and about 1.5 km downstream of the Otowi Bridge. Water flows from several discharge points, creating a marshy area with abundant grasses, and the combined total flow is ≤30 L/m (Figure E.9-1).

The bench from which the spring issues occurs within a landslide complex made up primarily of pale-pinkto-tan bedded pebble conglomerate, sandstone, siltstone, and mudstone of the Santa Fe Group (Figure E.9-2). Lithic fragments consist of quartz, microcline, gneiss, schist, granite, quartzite, and rare volcanics. About 20 m above the spring, the beds dip about 5° to the WNW. At the top of the complex and roughly 100 m to the west is another landslide block in which highly tilted columnar basalt overlies coarse boulder conglomerate of mostly quartzite and crystalline rocks. These lithologies belong to the Cerros del Rio volcanic field and Totavi Lentil.

# **E.10 UPPER CAÑON DE VALLE SPRING (TSHIREGE MEMBER, BANDELIER TUFF)**

**Location:** Bland 7.5 min USGS topo quad (Latitude N35˚51'32.38", Longitude W106˚22'47.09", Elevation 2569 m)

**Ownership:** U.S. Forest Service

#### **Geologic Map:** Smith et al. (1970, 09752)

**Description:** Upper Cañon de Valle spring issues about 6 m in front of a collapsed, wood-framed tunnel entrance (Figure E.10-1), about 2.4 km west of State Highway 501. The spring and tunnel are situated on a tiny bench on the north canyon wall, about 20 m above the bottom of upper Cañon de Valle. Measured flow rates of the spring are generally small (≤5 L/m). The horizontal penetration distance of the tunnel into the bedrock is not known.

The tunnel is constructed into pale-tan-to-gray, devitrified, densely welded Tshirege Member of the Bandelier Tuff. At this location, open horizontal and vertical joints break the tuff, forming slabs about 0.2 m thick. Some zones in the tuff contain cream-to-white lithophysal cavities up to 4 cm wide. The tuff is relatively crystal-rich with phenocrysts of clear quartz, chatoyant sanidine, and tiny black clinopyroxene. Lithic fragments are rare. Fiamme appear as white devitrified streaks.

About 50 m downstream of the spring, an outcrop of flow-banded porphyritic dacite (Tschicoma Formation) occurs along the north side of the canyon drainage. Another 200 m downstream is a 50-m-tall spire and an underlying talus pile of similar dacite. Thus, it appears that the Tshirege Member fills preexisting topography in the vicinity of the spring and that the thickness of tuff is not uniform.

# **E.11 WATER CANYON GALLERY (TSHIREGE MEMBER, BANDELIER TUFF)**

**Location:** Frijoles 7.5 min USGS topo quad (Latitude N35˚50'39", Longitude W106˚22'19", Elevation 2439 m)

**Ownership:** The U.S. Forest Service with water rights granted to the U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752), Goff et al. (2002a, 88776)

**Description:** Water Canyon Gallery is an improved spring occurring in the north branch of uppermost Water Canyon, about 1.3 km west of State Highway 501 and just west of the Pajarito Plateau. The spring issues from a horizontal tunnel about 1.3 m high and roughly 35 m long extending into a cliff of densely welded rhyolite tuff. Stone blocks flank the mouth of the tunnel, and the tunnel entrance is built at the top of a talus pile of tuff (Figure E.11-1). Water is collected in a 10-in.-diameter pipe inside the tunnel, and the pipe follows the canyon downhill. About 200 m southeast of the gallery, the pipe is disconnected, and spring water empties into the canyon bottom drainage (Figure E.11-2). The Laboratory's Technical Area 16 used the water previously. Flow rates during the last 20 years have varied from 50 to at least 200 L/min. (The 1989 annual average was 166 L/min [Stoker et al. 1992, 12017]; the annual average was 65 L/min [Purtymun et al. 1993, 15371]).

The tuff at the gallery consists of dark gray, densely welded, devitrified ignimbrite of the Tshirege Member of the Bandelier Tuff. The tuff at the gallery mouth is massive with broadly spaced vertical cooling joints and other open cracks. About 10 m above the spring is a discontinuous, up to 1-m-wide zone of open, horizontally flattened cavities resembling large vesicles (Figure E.11-3). These cavities may mark a flow unit boundary within Qbt4. No surge beds were found in the tuff immediately near the gallery. Above the zone of cavities, the tuff displays horizontal jointing.

Phenocrysts in the tuff consist of clear quartz and sanidine, the latter displaying chatoyancy. Tiny clinopyroxene phenocrysts are oxidized to orange iron (oxy)hydroxides. The tuff contains conspicuous fiamme but extremely rare lithic fragments.

# **E.12 GUAJE CANYON #5 WELL (SANTA FE GROUP)**

**Location:** Guaje Mountain 7.5 min USGS topo quad (Latitude N35˚54'51", Longitude W106˚13'37", Elevation 1926 m)

**Ownership:** U.S. Forest Service with water rights to U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752), Kempter and Kelley (2002, 88777)

**Total Drilled Depth:** 614 m

**Description:** Well G-5 was completed in May 1951 to a depth of 608.8 m (Purtymun 1995, 45344) and was reliably used as a water supply well until it was plugged and abandoned in 1998. The initial static water level was 125 m below surface but through time the water level has descended as a result of production and draw-down (148 m in 1991). The production rate was about 1960 L/min. The screened interval and production horizon of the well were entirely within the Santa Fe Group. Before being abandoned in 1998, the well was sampled from a faucet near the wellhead during pumping.

The stratigraphy at G-5 was formerly interpreted as valley-fill alluvium to 2.4 m, fanglomerate of the Puye Formation to 38.7 m, and interbedded sedimentary rocks, lavas, and volcanic breccias of the Santa Fe Group to total depth (Purtymun 1995, 45344, Table XXI-C, p. 273). No interval of coarse boulder conglomerate of the Totavi Lentil is reported between the Puye Formation and the Santa Fe Group. In older reports, the sediments of the Santa Fe Group are generally assigned to the Chamita and Tesuque Formations (Baltz et al. 1963, 08402; Manley 1979, 11714). Purtymun (1995, 45344), however, reassigned the sedimentary sequence partly to the "Chaquehui Formation" (38.7 to 369.2 m) and to the Tesuque Formation (405.5 m to total depth). An interval of interbedded basalt and/or breccia from 369.2 to 405.5 m forms a boundary between the two units.

The current interpretation of G-5 stratigraphy keeps most of Purtymun's units but recognizes that the deposits from 38.7 m to 369.2 m are fanglomerates unrelated to the phreatomagmatic deposits of Chaquehui Canyon; this interval at G-5 represents deposits now referred to informally as "older fanglomerate" that is more similar to the overlying Puye Formation.

# **E.13 LAOI(A)-1.1 WELL (GUAJE PUMICE BED, OTOWI MEMBER, BANDELIER TUFF)**

**Location:** Guaje Mountain 7.5 minute USGS topo quad (Latitude N35° 52' 31.6", Longitude W106°17' 13.5", Elevation 2084 m)

**Ownership:** U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752), Kempter and Kelley (2002, 88777)

#### **Total Drilled Depth:** 98.5 m

**Description:** Well LAOI(A)-1.1 is an observation well that was drilled in upper Los Alamos Canyon in 1994. It contains a 3-in.-diameter schedule-80 PVC casing and is screened to accept water from a perched zone in the Guaje Pumice Bed at the base of the Otowi Member of the Bandelier Tuff (Figure E.13-1). The Guaje Pumice Bed is about 6.7 m thick at this location. The well actually penetrated the top of the Puye Formation at 96 m depth, but the hole in the Puye section collapsed. Three wellbore volumes, or about 55 gal. of water, are withdrawn before each sampling round, using nitrogen gas and a bladder pump. Most water originates from an approximate depth of 94.5 m.

# **E.14 LAO-B WELL (VALLEY-FILL ALLUVIUM OF TSCHICOMA FORMATION AND TSHIREGE MEMBER, BANDELIER TUFF)**

**Location:** Guaje Mountain 7.5 min USGS topo quad (Latitude N35°52' 43.8", Longitude W106° 20' 7.1", Elevation 2233 m)

**Ownership:** U.S. Department of Energy

**Geologic Map:** Smith et al. (1970, 09752); Kempter and Kelley (2002, 88777)

**Total Drilled Depth:** 5.61 m

**Description:** Well LAO-B is an observation well drilled into valley-fill alluvium in upper Los Alamos Canyon. The casing diameter is about 4 in. (Figure E.14-1). Rocks penetrated consist of boulders, cobbles, and pebbles of porphyritic dacitic rocks of the Tschicoma Formation and nonwelded-to-welded rhyolitic tuff of the Tshirege Member of the Bandelier Tuff in a volcanic sand-to-silt matrix. Three wellbore volumes, or about 40 gal. of water, are withdrawn before each sampling round using an air compressor and bladder pump. The groundwater originates from the bottom of the well.

# **E.15 OTOWI #4 WELL (SANTA FE GROUP)**

**Location:** Frijoles 7.5 min USGS topo quad (Latitude N35˚52'22", Longitude W106˚15'35", Elevation 2020 m)

**Ownership: U.S. Department of Energy** 

**Geologic Map:** Smith et al. (1970, 09752), Goff et al. (2002, 88776)

**Total Drilled Depth**: 855.5 m

**Description:** Otowi-4 is a water supply well that was completed to a final depth of 788.1 m in March 1990 (Stoker et al. 1992, 12017). The well is one of several intended to replace less productive and much older water supply wells in Los Alamos and Guaje Canyons. The well contains a 16-in.-diameter screen from 340 to 785 m. The static water level is about 241 m below the surface, and the well produces about 5600 L/min when in use. In late 1999 and early 2000, Otowi-4 was temporarily out of service for repairs. The well is sampled from a faucet near the wellhead during pumping.

In earlier work, the stratigraphy of Otowi-4 has been described by Stoker et al. (1992, 12017, Table VIII), with stratigraphy later modified by Purtymun (1995, 45344). The current stratigraphic interpretation is shown in Figure E.15-1. In this figure "Tf" represents the older fanglomerate, as discussed in section E.12 (Well G-5). Aside from a section of Miocene Basalts, the screened interval at Otowi-4 is entirely within the older fanglomerates, from 340 m (1115 ft) to 785 m (2575 ft) depth.



**Figure E.1-1. Photograph of Apache Spring taken April 27, 2000; the temperature is 18°C, and the flow rate is 0.45 L/min.** 



**Figure E.1-2. Photograph of flow-banded dacite lava along trail about 10 m above Apache Spring.** 



**Figure E.2-1. Photograph looking toward the northwest wall of White Rock Canyon showing the location of Spring 9B relative to the local geology. The spring issues from the approximate contact of basaltic hydromagmatic (maar) deposits and an overlying basalt flow. At least two more basalt lavas are interbedded with thin intervals of maar deposits (symbol B/M, located on uppermost basalt). The lava sequence is capped by a thick benmoreite flow (Ben).** 



**Figure E.2-2. Photograph of Spring 9B taken May 5, 2000; the temperature is 15°C, and the flow rate is <0.3 L/min. A hammer straddles the contact between the basal lava breccia and the underlying hydromagmatic deposits.** 



**Figure E.2-3. Close-up photograph of hydromagmatic (maar) deposits about 5 m below and north of Spring 9B. Note large bomb sag (to the left of the hammer) in crossbedded sandstone to mudstone, caused by the impact of the basalt bomb.** 



**Figure E.3-1. Photograph of primary sampling point at Doe Spring taken May 5, 2000; the temperature is 17°C, and the flow rate is 0.2 L/min.** 



**Figure E.4-1. Photograph looking east of landscape at La Mesita Spring. The Rio Grande is in the foreground. The basalt of Buckman Mesa appears in the right skyline.** 



**Figure E.4-2. Photograph of La Mesita Spring taken May 4, 2000; the temperature is 19°C, and the flow rate is 0.5 L/min** 



**Figure E.5-1. Photograph of sampling point at Pajarito Spring (Spring 4A) taken April 28, 2000; the temperature is 19°C, and the flow rate is 120 L/min (±25%).** 



**Figure E.5-2. Photograph of disturbed geology in the lower part of the landslide block hosting Pajarito Spring. Intact 1-m-wide chunk of bedded siltstone of the Santa Fe Group (SF) is incorporated into a jumbled mixture of sandstone and basalt blocks (B).** 



**Figure E.5-3. Photograph of lithologies in the upper part of the landslide block hosting Pajarito Spring. A tilted layer of rounded cobbles resembling lithologies in the Totavi Lentil is sandwiched between layers of angular basalt rubble.** 



**Figure E.6-1. Photograph of Pine Spring taken May 4, 2000; the temperature is 21°C, and the spring is not flowing** 



**Figure E.6-2. Photograph of weathered, fractured andesite lava exposed in bluff downstream and east of Pine Spring.** 



**Figure E.7-1. Photograph of Sacred Spring taken on May 4, 2000; the temperature is 20°C, and the flow rate is 2 L/min** 



**Figure E.7-2. Photograph of landscape northeast of Sacred Spring. Gray volcaniclastic rocks of the Puye Formation (P) form bluffs overlying pale-pink sedimentary rocks of the Santa Fe Group (SF).** 



**Figure E.8-1. Photograph of the largest discharge point at Seven Springs taken April 27, 2000; the temperature is 15°C, and the flow rate is 6 L/min (±10%). The water issues from a vertical crack in a horizontally foliated and welded Otowi Member of the Bandelier Tuff.** 



**Figure E.9-1. Photograph of Spring 1 taken May 4, 2000; the temperature is 10°C, and the flow rate is approximately 20 L/min** 



**Figure E.9-2. Photograph of bedded sandstone and siltstone in the Santa Fe Group about 20 m above Spring 1. The sediments and overlying rubble of basalt are part of a landslide block from which the spring issues.** 



**Figure E.10-1. Photograph of Upper Cañon de Valle Spring taken on April 29, 2000; the temperature is 15°C, and the flow rate is 0.8 L/min** 



**Figure E.11-1. Photograph of the entrance to Water Canyon Gallery taken on April 27, 2000** 



**Figure E.11-2. Photograph of disconnected discharge pipe from Water Canyon Gallery taken April 27, 2000; the temperature is 14°C, and the flow rate is 120 L/min (±25%)** 



**Figure E.11-3. Photograph of vesicular cavities in a flow unit of densely welded Tshirege Member, Bandelier Tuff, about 10 m above the entrance to Water Canyon Gallery** 



**Figure E.13-1. Stratigraphy and completion diagram of LAOI(A)-1.1 well** 



**Figure E.14-1. Completion diagram of LAO-B well** 



**Figure E.15-1. Diagram showing the lithology of Otowi-4. Unit symbols are shown for the Puye Formation (Tpf), Cerros del Rio lavas (Tb4), pumiceous deposits (Tpp), river gravels related to the Totavi (Tpt), older fanglomerates (Tf), Miocene basalts (Tb2), and possible transition into sands of the Santa Fe Group (Ts) at depth. The screen depth is from 1115 ft to 2575 ft.** 

# **Appendix F**

*Interlaboratory Comparison Data*
# **Figures**



### **F.1 STANDARD OPERATING PROCEDURES**

This section presents a summary of the SOPs used by EES-6. Analytical instruments and their application for sample characterization are listed to provide the basis of selecting EES-6 for screening analyses during this investigation. Analytical methods used during this investigation included ICPAES, GFAA, cold vapor atomic absorption (CVAA), IC, ISE, alkalinity titration, and gaseous hydride generation atomic absorption (GHAA) spectroscopy.

### **F.1.1 Elements by ICP Atomic Emission Spectroscopy**

LANL-EES-1-SOP-01.1, R0 describes the procedure used in determining the following elements by ICPAES: aluminum, boron, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, lead, silicon, silver, strontium, titanium, vanadium, and zinc. This method is comparable to SW-846 Method 6010A and EPA Method 200.7 (EPA 1987, 31732).

The following equipment may be used and will be controlled in accordance with LANL-EES6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- ICPAES: Leeman's Model PS1000UV ICP Emission Spectrophotometer (PN 738144) and the following accessories:
	- ♦ autosampler
	- ♦ integrated software for system control and data management
	- ♦ Questron Qwave 3000 microwave (PN 971309)
	- ♦ Mettler PE 1600 balance (PN 624733)
	- ♦ Mettler AE 240 balance (PN 656788)
	- ♦ pipettes and appropriate lab ware

This SOP applies to samples requiring ICPAES for work under the EES Quality Management Plan (QMP) by EES-6 personnel. Any sample that can be put into a solution and for which the element concentrations are within the instrument's detection range can be analyzed by ICPAES. Elements that have detection limits insufficient for the samples being analyzed must be determined using alternative methods, such as GFAA or GHAA.

### **F.1.2 Elements by Graphite Furnace Atomic Absorption Spectroscopy**

LANL-EES-1-SOP-01.2, R0 describes the procedure used for analyzing the following trace elements by GFAA spectroscopy: antimony, arsenic, cadmium, cobalt, chromium, cesium, copper, molybdenum, nickel, lead, rubidium, selenium, silver, tin, and thallium. This SOP is comparable to EPA Method 200.9 (EPA 1987, 31732).

The following equipment may be used and will be controlled in accordance with LANL-EES6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- Perkin Elmer Model 5500 Atomic Absorption Spectrophotometer with continuum background corrector (PN 487640) and the following accessories:
	- ♦ Model HGA 500 furnace accessory (PN 487638)
	- ♦ AS40 autosampler (PN 733079)
- ♦ single or multielement hollow cathode lamps, or electrode discharge lamps (EDLs) (PN 834654) with Perkin Elmer system 2 power supply
- ♦ Perkin Elmer 7700 computer system (PN 656260) with HGA Graphics II data software
- ♦ Questron Qwave 3000 microwave (PN 971309)
- ♦ Mettler PE 1600 Balance (PN 624733)
- ♦ Mettler AE 240 Balance (PN 656788)
- ♦ pipettes and appropriate lab ware

This SOP applies to samples, with low-level concentrations of dissolved elements, requiring GFAA for work under the EES-QMP. Any sample that can be put into a solution and for which the sample matrix does not create an interference that cannot be compensated for by background correction or matrix modification can be analyzed by GFAA.

### **F.1.3 Elements by Gaseous Hydride Atomic Absorption Spectroscopy**

LANL-EES-1-SOP-01.3, R0 describes the procedure used for analyzing the following elements by GHAA: antimony, arsenic, and selenium. This SOP is comparable to SW-846 Methods 7062 and 7742 (EPA 1986, 31732).

The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- Perkin Elmer Model 5500 Atomic Absorption Spectrophotometer (PN 487640) and the following accessories:
	- ♦ Single or multielement hollow cathode lamps, or EDL (PN 834654) with Perkin Elmer System 2 power supply
	- ♦ Perkin Elmer 7700 computer system (PN 656260) with HGA Graphics II data software
	- ♦ Cold-vapor/hydride generator, Perkin Elmer Model MHS-10 (PN 838904)
	- ♦ Argon, acetylene, and compressed air
	- ♦ Questron Qwave 3000 microwave (PN 971309)
	- ♦ Mettler PE 1600 balance (PN 624733)
	- ♦ Mettler AE 240 balance (PN 656788)
	- ♦ pipettes and appropriate lab ware

This SOP applies to liquid, solid, and slurry samples requiring GHAA for work under the EES-QMP.

### **F.1.4 Cold Vapor Atomic Absorption Spectroscopy**

LANL-EES-1-SOP-01.4, R0 describes the equipment used for CVAA analysis of the organic and inorganic mercury in aqueous, solid, and semisolid samples. This SOP is comparable to SW-846 Methods 7470A and 7471A and EPA Method 245.1 (EPA 1987, 31732).

The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:

• Perkin Elmer Model 5500 Atomic Absorption Spectrophotometer (PN 487640) and the following accessories:

- ♦ single or multielement hollow cathode lamps, or EDLs (PN 834654) with Perkin Elmer System 2 power supply.
- ♦ Perkin Elmer 7700 computer system (PN 656260) with HGA Graphics II data software
- ♦ cold-vapor/hydride generator, Perkin Elmer Model MHS-10 (PN 838904)
- ♦ Questron Qwave 3000 microwave (PN 971309)
- ♦ Mettler PE 1600 balance (PN 624733)
- ♦ Mettler AE 240 balance (PN 656788)
- ♦ pipettes and appropriate lab ware
- ♦ argon gas

This SOP applies to liquid, solid, and slurry samples to be analyzed under the EES-QMP.

### **F.1.5 Alkalinity Titration**

LANL-EES-1-SOP-01.8, R0 describes the procedure used for determining alkalinity in water samples and reporting this alkalinity as bicarbonate, carbonate, and hydroxide, or as total alkalinity, as applicable.

The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- Mettler DL25 Titrator (PN 843449) and the following accessories:
	- ♦ Mettler ST20 sample changer
	- ♦ printer
	- ♦ combination pH electrode
	- ♦ automatic temperature compensator probe
	- ♦ Mettler PE 1600 balance (PN 624733)
	- $\bullet$  pipettes and appropriate lab ware

This SOP applies to aqueous solutions with a pH above the bicarbonate endpoint to be analyzed under the EES QMP.

#### **F.1.6 Specific Conductance**

LANL-EES-1-SOP-01.7, R0 describes the procedure used to determine the specific conductance of a solution using an Orion Model 160 Conductivity meter and an Orion Model 016010 Electrode conductivity cell.

The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- conductivity meter, Orion Model 160 (S/N 23637032)
- 4-electrode conductivity cell, Orion Model 016010

This SOP applies to aqueous samples requiring a conductivity measurement for work under the EES-QMP.

## **F.1.7 Ion Chromatography**

LANL-EES-1-SOP-01.5, R0 describes the procedure used for preparing and analyzing the following analytes for IC, including: fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate, iodide, chlorate, perchlorate, thiosulfate, and thiocyanate. Other analytes may be included if their characteristics make them amenable to this SOP. This SOP is comparable to SW-846 Method 9056 and EPA Method 300.0 (EPA 1987, 31732).

The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:

- Ion Chromatograph, Dionex Model 4000 and 4500i with conductivity and ultraviolet/visible (UV/Vis) detectors and the following accessories:
	- ♦ Dionex AutoIon 450 data system
	- ♦ automated sampler
	- ♦ suppressor system
	- ♦ ion exchange columns
	- ♦ pipettes and appropriate labware

This SOP applies to aqueous samples, or samples that through pretreatment can be made aqueous, requiring IC for work under the EES-QMP.

### **F.1.8 Ion-Selective Electrode Measurements**

LANL-EES-1-SOP-01.10, R0 describes the procedure used for measuring the concentration of the following ions in solution using electrochemical sensors: ammonium, fluoride, and sulfide. The potential for the electrochemical sensors varies with the logarithm of the ion's activity in solution.

- The following equipment may be used in this SOP and will be controlled in accordance with LANL-EES-6-AP-01.11, Control of Measuring and Test Equipment and Standards:
	- ♦ Orion combination fluoride electrode, model 96-09
	- ♦ Orion ammonium electrode, model 95-12
	- ♦ Orion silver/sulfide electrode, model 94-16
	- ♦ Orion double junction reference electrode, model 90-02
	- ♦ magnetic stirrer

This SOP applies to solutions requiring ammonium, fluoride, and sulfide measurements for work under the EES-QMP.

### **F.2 EES AND PARAGON ANALYTICS, INC. COMPARISONS**

Apache Spring was sampled six times during the course of this investigation. Analytical results (trace elements) for duplicate samples analyzed by both EES-6 and Paragon Analytics, Inc. during February 1998 are provided in Figure F.2-1. Method-detection limits are lower for those trace elements (arsenic, cadmium, cobalt, and nickel) analyzed by AA methods compared to the same elements analyzed by the ICPAES method, as shown in Figure F.2-1. The units of mg/L and ppm are equivalent in these low-ionicstrength waters. Sample results reported by Paragon Analytics, Inc. showed some inconsistencies in detection limits inherent from the ICPAES method (Figure F.2-1). Paragon Analytics, Inc. reported higher concentrations of aluminum, iron, manganese, and vanadium compared to EES-6 results for this

sampling event, but there is good agreement between the two laboratories for barium, lead, and strontium.

Figure F.2-2 shows an excellent comparison between analytical results for major cations reported by EES-6 and Paragon Analytics, Inc. for alluvial well LAO-B sampled in February and October 1998. Concentrations of calcium, potassium, magnesium, and generally sodium are within analytical uncertainties measured by each laboratory and data plot on or close to the line characterized by a 1:1 slope (exact agreement). Both laboratories used the ICPAES method for the major ion analysis. There is some variation in solute concentrations for well LAO-B, reflecting both short residence time within alluvial groundwater and variation in surface water chemistry. During 1998, concentrations of calcium, magnesium, potassium, and sodium were lower in February than those reported for the October samples.

Figure F.2-3 also shows an excellent agreement between analytical results for major ions provided by NMED-OB, Paragon Analytics, Inc., and EES-6 for groundwater samples collected from La Mesita Spring during April and July 1998. There is very little variation in major ion chemistry at this spring, which is the result of long residence times for groundwater in the regional aquifer.

Figure F.2-4 is a plot of analytical results for major ions and TDS reported by both EES-6 and Paragon Analytics, Inc. for duplicate groundwater samples collected at Apache Spring during February 1998. For most of the major ions, there is an excellent agreement in analytical results reported by the two laboratories. The EES-6 analytical laboratory, however, reported a bicarbonate concentration of 65 ppm, but Paragon Analytics, Inc. reported a value of 54 mg/L for this sampling event. Discrepancy in the reported bicarbonate concentrations could be due to carbon dioxide gas diffusion from the sample bottle sent to Paragon Analytics, Inc. (analyzed one to two weeks later than EES-6), resulting in a lower bicarbonate concentration. The EES-6 laboratory also reported higher TDS of 175 ppm (or mg/L) as compared to Paragon's reported value of 160 mg/L, which is reflected by the higher bicarbonate concentration.

Figure F.2-5 shows an excellent comparison of analytical results between Paragon Analytics, Inc. and EES-6 for major ion concentrations at Doe Spring sampled in February and September 1998. Concentrations of calcium and sodium show some variation within one to two mg/L or ppm. Calcium concentrations were slightly higher in February 1998, but sodium concentrations were higher in September 1998. There is very little variation in analyte concentrations for chloride, magnesium, potassium, and sulfate measured during the two sampling events, suggesting a longer residence time for intermediate perched groundwater discharging at Doe Spring as compared to alluvial groundwater (LAO-B).



**Figure F.2-1. Comparison of trace element chemistries reported by EES-6 and NMED for Apache Spring (Tschicoma Formation) sampled in February 1998** 



**Figure F.2-2. Comparison of major ion chemistries reported by EES-6 and Paragon Analytics, Inc. for well LAO-B (alluvium) in February and October 1998** 



**Figure F.2-3. Comparison of major ion chemistries reported by EES-6, Paragon Analytics, Inc., and NMED for La Mesita Spring (Santa Fe Group) sampled in April and July 1998** 



**Figure F.2-4. Comparison of major ion chemistries and total dissolved solids reported by EES-6 and NMED for Apache Spring (Volcanics) sampled in February 1998** 



**Figure F.2-5. Comparison of major ion chemistry (dissolved) reported by EES-6 and Paragon Analytics, Inc. for DOE Spring (Basalt) sampled in February and September 1998** 

**Table A-1 Post-1997 Samples and Types of Analyses** 

Location	Prep	<b>Type</b>	Date <b>MM/DD/YY</b>	Event	Groundwater Sample ID	Sample ID	<b>Sample ID and Method</b>	<b>Request Numbers</b>	organics غ	<u>က</u> ш Inorganics	Rads	Tritium	တ <u>ئە</u> Gross	Rads G-Scan	Other	(၁၀) Temp	ce (µS/cm) Specific <u>ian</u> Average Conduct	玉	Turbidity (NTU)
Apache Spring	filtered	sample	5/7/1997		PP97-07	PP97-7	PP97-7 filtered	°na	$^{\circ}$ O	$\mathbf{c}_{\mathbf{X}}$	$\circ$	X	o	$\Omega$	х	8.3	199	7.27	$\mathbf 0$
Apache Spring	filtered	original	8/6/1997	$\overline{2}$	PP97-29	0816-97-1043	0816-97-1043 filtered	3513R, 3514R	$\circ$	x	X	$\circ$	$\circ$	X	х	8.6	$\frac{d}{}$	7.26	$\overline{\phantom{0}}$
Apache Spring	filtered	duplicate <sup>a</sup>	8/6/1997	$\overline{2}$	PP97-30	0816-97-1044	0816-97-1044 filtered	3513R, 3514R	$\circ$	x	X	$\circ$	o	$\boldsymbol{\mathsf{x}}$	X	8.6		7.26	$\overline{\phantom{0}}$
Apache Spring	filtered	sample	8/6/1997	$\overline{2}$	PP97-30	PP97-30	PP97-30 filtered	(lab sample #0816-97-1044)	$\circ$	$\boldsymbol{\mathsf{x}}$	$\circ$	X	$\circ$	$\Omega$	х	8.6	$\overline{\phantom{0}}$	7.26	$\qquad \qquad -$
Apache Spring	filtered	sample	2/9/1998	-3	PP98-05	0816-98-0009	0816-98-0009 filtered	4094R, 4095R, 4097R	X	х	X	$\circ$	X	$\boldsymbol{\mathsf{x}}$	X	6.5	165	7.96	5
Apache Spring	filtered	sample	7/1/1998	-5	PP98-20	RE16-98-9025	RE16-98-9025 filtered	4384, 4385R, 4387R	X	$\boldsymbol{\mathsf{x}}$	X	$\circ$	$\boldsymbol{\mathsf{x}}$	$\boldsymbol{\mathsf{x}}$	х	9.1	130	7.32	23.8
Apache Spring	filtered	duplicate	1/5/2000	$\overline{7}$	<b>PP00-1</b>	CABG-00-0012	CABG-00-0012 filtered	6303R, 6304R, 6302R	$\mathsf{x}$	x	$\circ$	$\circ$	O	$\Omega$	х	6	135	9.15	3.1
Apache Spring	filtered	original	1/5/2000	$\overline{7}$	PP00-2	CABG-00-0013	CABG-00-0013 filtered	6303R, 6304R, 6302R	X	x	$\circ$	$\circ$	$\circ$	$\Omega$	х	6	135	9.15	3.1
Apache Spring	filtered	sample	3/29/2000	8	PP00-16	CABG-00-0047	CABG-00-0047 filtered	6635R, 6634R, 6637R, 6636R	X	$\circ$	$\circ$	$\circ$	$\circ$	$\Omega$	х	7.6	280	7.33	7.3
Doe Spring	filtered	sample	4/22/1997		PP97-01	PP97-1	PP97-1 filtered		$\circ$	x	$\circ$	X	0	$\Omega$	х	17.5		8.19	$\overline{\phantom{0}}$
Doe Spring	filtered	sample	8/18/1997	2	PP97-36	0816-97-1051	0816-97-1051 filtered	3586R	$\circ$	x	X	$\circ$	o	$\boldsymbol{\mathsf{x}}$	х	20.2	51	8.27	0
Doe Spring	filtered	sample	2/3/1998	3	PP98-01	0816-98-0002	0816-98-0002 filtered	4079R,4082R	$\mathsf{x}$	x	X	$\circ$	X	$\boldsymbol{\mathsf{x}}$	х	13.8	120	8.12	15.3
Doe Spring	filtered	sample	9/23/1998	6	PP98-31	RE16-98-9006	RE16-98-9006 filtered	4695R, 4696R	$\mathsf{x}$	x	X	$\circ$	X	$\boldsymbol{\mathsf{x}}$	X	21	167	7.71	$\overline{\phantom{0}}$
Doe Spring	filtered	duplicate	1/7/2000	7	<b>PP00-7</b>	CABG-00-0018	CABG-00-0018 filtered	6320R, 6319R, 6321R	$\mathsf{x}$	x	$\circ$	$\circ$	O	$\Omega$	х	12.2	135	8.54	3.5
Doe Spring	filtered	original	1/7/2000	$\overline{7}$	PP00-8	CABG-00-0019	CABG-00-0019 filtered	6320R, 6319R, 6321R	$\mathsf{x}$	$\boldsymbol{\mathsf{x}}$	$\circ$	$\circ$	$\circ$	$\Omega$	x	12.2	135	8.54	3.5
Doe Spring	filtered	sample	4/6/2000	8	PP00-36	CABG-00-0059	CABG-00-0059 filtered	6700R, 6699R, 6698R, 6701R	$\mathsf{x}$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	X	15.7	80	6.89	7.4
Guaje #5	filtered	original	5/29/1997		PP97-18	PP97-18	PP97-18 filtered		$\circ$	X	$\circ$	X	$\circ$	$\circ$	х	26.8	186	7.86	
Guaje #5	filtered	duplicate	5/29/1997		PP97-19	PP97-19	PP97-19 filtered	—	$\circ$	x	$\circ$	X	$\circ$	$\Omega$	х	26.8	186	7.86	$\overline{\phantom{0}}$
Guaje #5	filtered	sample	8/19/1997	$\overline{2}$	PP97-37	0816-97-1100	0816-97-1100 filtered	3603R	$\circ$	x	X	$\circ$	O	$\boldsymbol{\mathsf{x}}$	х	26.4	216	6.81	0
Guaje #5	filtered	sample	9/28/1998	6	PP98-34	RE16-98-9010	RE16-98-9010 filtered	4714R, 4715R, 4716R	X	x	X	$\circ$	x	X	х	24.2	190	8.11	0.55
La Mesita Spring	filtered	sample	5/21/1997		PP97-15	PP97-15	PP97-15 filtered		$\circ$	x	$\circ$	X	o	$\Omega$	х	15.2	285	7.17	0
La Mesita Spring	filtered	sample	8/5/1997	$\overline{2}$	PP97-27	0816-97-1039	0816-97-1039 filtered	3489R, 3490R	$\circ$	х	х	$\circ$	O	x		16.6		6.5	$\overline{\phantom{0}}$
La Mesita Spring	filtered	sample	4/7/1998		PP98-15	0816-98-0047	0816-98-0047 filtered	4204R, 4205R, 4207R	$\boldsymbol{\mathsf{x}}$		x	$\Omega$	X	x		12.5	320	7.4	7.6
La Mesita Spring	filtered	sample	7/7/1998	5	PP98-26	PP98-26	PP98-26 filtered	(lab sample #RE16-98-9015 filtered)	$\circ$	$\circ$	$\circ$	$\boldsymbol{\mathsf{x}}$	$\circ$	$\circ$	$\boldsymbol{\mathsf{x}}$	15	230	7.48	9.3
La Mesita Spring	filtered	original	7/7/1998	5	PP98-25	RE16-98-9014	RE16-98-9014 filtered	4403R, 4404R, 4405R	$\mathsf{x}$	x	X	$\circ$	X	$\boldsymbol{\mathsf{x}}$	х	15	230	7.48	9.3
La Mesita Spring	filtered	duplicate	7/7/1998	5	PP98-26	RE16-98-9015	RE16-98-9015 filtered	4403R, 4404R, 4405R	X	х	X	$\circ$	X	X	X	15	230	7.48	9.3
La Mesita Spring	filtered	sample	12/16/1999	-7	<b>PP99-4</b>	CABG-99-0006	CABG-99-0006 filtered	6266R, 6265R, 6267R	$\mathsf{x}$	x	$\circ$	$\circ$	$\circ$	$\circ$	x	12.5	330	8.13	10.4
La Mesita Spring	filtered	sample	4/10/2000	8	PP00-40	CABG-00-0056	CABG-00-0056 filtered	6707R, 6706R, 6708R, 6705R	$\mathsf{x}$	$\circ$	$\circ$	$\circ$	$\circ$	$\circ$	X	15	220	6.37	4.3
LAO-B	filtered	sample	5/14/1997		<b>PP97-13</b>	PP97-13	PP97-13 filtered	$\overline{\phantom{m}}$	$\circ$	X	$\circ$	X	o	$\circ$	X	4.8	105	6.64	0
LAO-B	filtered	original	8/1/1997	$\overline{2}$	PP97-21	0816-97-1029	0816-97-1029 filtered	3481R, 3482R	$\circ$	X	X	$\mathsf{o}$	o	X	X	9.6	98	6.79	
LAO-B	filtered	duplicate	8/1/1997	$\overline{2}$	PP97-22	0816-97-1030	0816-97-1030 filtered	3481R, 3482R	o	X	X	$\mathsf{o}$	o	X	X	9.6	98	6.79	















#### EES **Inorganics EES**  Inorganics **Inorganics Tritium Rads Date Groundwater MM/DD/YY Sample ID Sample ID Sample ID and Method Request Numbers** Location | Prep | Type Event Upper Cañon de Valle Spring nonfiltered sample 5/13/1997 1 PP97-12 PP97-12 PP97-12 nonfiltered — o x o o o o x 8.9 70 7.33 0 Upper Cañon de Valle Spring nonfiltered sample 8/4/1997 2 PP97-23 0816-97-1031 0816-97-1031 nonfiltered 3485R o x x o o x x 8.2 94 7.3 0 (lab sample #0816-97-1031 raw, Upper Cañon de Valle Spring **nonfiltered** sample 8/4/1997 2 PP97-23 PP97-23 PPP97-23 nonfiltered -1032 filtered) o o o x o o x 8.2 94 7.3 0 Upper Cañon de Valle Spring |nonfiltered |sample |2/23/1998 | 3 |PP98-10 |0816-98-0034 |0816-98-0034 nonfiltered |4127R, 4129R, 4130R x x x x x x x x 8.7 | 80 | 8.04 | 1.4 Upper Cañon de Valle (lab sample #0816-98-0034 raw, Spring and nonfiltered sample 2/23/1998 3 PP98-10 PP98-10 PP98-10 nonfiltered -0035 filtered) | o | o | o | x | o | o | x | 6.7 | 80 | 8.04 | 1.4 Upper Cañon de Valle (lab sample #RE16-98-9028 raw and Spring **nonfiltered** sample 7/1/1998 5 PP98-19 PP98-19 PP98-19 PP98-19 nonfiltered -9029 filtered) o o o x o o x 7.3 65 7.76 4.6 Upper Cañon de Valle Spring and and the profiltered sample 7/1/1998 5 PP98-19 RE16-98-9028 RE16-98-9028 nonfiltered 4384R, 4387R x x x x o Upper Cañon de Valle Spring and intered sample 1/5/2000 7 PP00-4 CABG-00-0004 CABG-00-0004 nonfiltered 6307R, 6305R, 6306R o o o x Upper Cañon de Valle Spring and sample  $\overline{a}$  and  $\overline{a}$ Water Canyon Gallery |nonfiltered |sample |5/7/1997 | 1 |PP97-08 |PP97-8 POINTered | and the sample | the sample | 5/7/1997 | 1 |PP97-08 | PP97-8 nonfiltered | and the sample | the sample | 5/7/1997 | 1 | PP97-08 | PP97-8 Water Canyon Gallery |nonfiltered |sample |8/6/1997 | 2 |PP97-28 | 0816-97-1040 |0816-97-1040 nonfiltered |3514R 1 .2 | 7.21 | (lab sample #0816-97-1040 raw, Water Canyon Gallery nonfiltered sample 8/6/1997 2 PP97-28 PP97-28 PP97-28 PPP97-28 Ponfiltered -1041 filtered) | o | o | o | x | o | o | x | 11.2 | — | 7.21 | — Water Canyon Gallery |nonfiltered |sample |2/9/1998 | 3 |PP98-03 |0816-98-0005 |0816-98-0005 nonfiltered |4094R, 4096R, 4097R | x | x | x | x | x | x | x | 11.1 | 90 | 7.74 | 1.8 (lab sample #0816-98-0005 and Water Canyon Gallery |nonfiltered |sample |2/9/1998 | 3 |PP98-03 | PP98-3 | PP98-3 nonfiltered -0052 raw, -0006 and -0053 filtered) o o o x o o x 11.1 90 7.74 1.8 (lab sample #RE16-98-9026 raw and Water Canyon Gallery nonfiltered sample 7/8/1998 5 PP98-28 PP98-28 PP98-28 PP98-28 Ponfiltered -9027 filtered) | o | o | o | x | o | o | x | 10.8 | 65 | 7.23 | 1.7 Water Canyon Gallery  $\vert$ nonfiltered sample 7/8/1998 | 5 PP98-28 RE16-98-9026 RE16-98-9026 nonfiltered 4411R, 4413R  $\vert x \vert x \vert x$  x x o Water Canyon Gallery nonfiltered sample 1/5/2000 7 PP00-3 CABG-00-0003 CABG-00-0003 nonfiltered 6307R, 6305R, 6306R Water Canyon Gallery  $|$ nonfiltered  $|$ sample  $|3/30/2000$   $|$  8  $|$ PP00-19  $|$  CABG-00-0031  $|$ CABG-00-0031 nonfiltered  $|6645R,6647R$   $|$  o  $|$  o  $|$  o  $|$  x  $|$

Water Canyon Gallery nonfiltered sample  $3/30/2000$  8 PP00-20 CABG-00-0032 CABG-00-0032 nonfiltered 6645R, 6647R o o o x

**Table A-1 (continued)** 



Note: The LAO-B post Cerro Grande Fire samples are not included in this table.

 $a$  duplicate = field duplicate of the original sample; sample = sample not paired with another sample ID.

 $<sup>b</sup>$  na = not available</sup>

 $\degree$  x = analyzed; o = not analyzed

 $d =$  = not measured

## **Table of Contents**

## **Location by Metals**



# **Location by Other Analytes**



# **Location by Radionuclides**



#### **Table B-1.1**

**Spring 1** 



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

 $\mathbf{U}$  = Not detected.

 $c$  na = Not analyzed.

#### **Table B-1.2 Sacred Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

 $b$  na = Not analyzed.

 $\ddot{U}$  = Not detected.

### **Table B-1.3 Otowi #4**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

<sup>b</sup> U = Not detected.<br><sup>c</sup> R = Rejected.

<sup>d</sup> na = Not analyzed.

### **Table B-1.4 La Mesita Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b U = Not detected.

 $c$  na = Not analyzed.

### **Table B-1.5 Guaje #5**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b na = Not analyzed.

<sup>c</sup> U = Not detected<br><sup>d</sup> R = Rejected.

#### **Table B-1.6 Water Canyon Gallery**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b na = Not analyzed.

 $\degree$  U = Not detected.

 $R =$  Rejected.

### **Table B-1.7 Upper Cañon de Valle Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

<sup>b</sup> U = Not detected.<br><sup>c</sup> na = Not analyzed.

 $d$  R = Rejected.

### **Table B-1.8 Spring 9b**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b U = Not detected.

 $c$  na = Not analyzed.

#### **Table B-1.9 Seven Springs**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

### **Table B-1.10 Pine Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b na = Not analyzed.

 $\degree$  U = Not detected.

 $R =$  Rejected.

### **Table B-1.11 Pajarito Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

### **Table B-1.12 LAOI-1.1(A)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

<sup>b</sup> na = Not analyzed.

 $c$  R = Rejected.

 $d$  U = Not detected.

### **Table B-1.13 Doe Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis b na = Not analyzed.

 $\degree$  U = Not detected.

### **Table B-1.14 Apache Spring**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TUICPMS = Total uranium inductively-coupled plasma mass spectrometry

TULIKPA = Total uranium kinetic phosphorimetric analysis

 $b$  na = Not analyzed.

 $\degree$  U = Not detected.

 $\textsf{d}$  R = Rejected.

### **Table B-1.15 LAO-B**


## **Table B-1.15 — LAO-B (continued)**



### **Table B.1-15 LAO-B (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

TULIKPA = Total uranium kinetic phosphorimetric analysis

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $R =$  Rejected.

### **Table B-2.1 Spring 1**



## **Table B-2.1 — Spring 1 (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

#### **Table B-2.2 Sacred Spring**



## **Table B-2.2 — Sacred Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

 $b$  na = Not analyzed.

 $\text{U} = \text{Not detected}.$ 

#### **Table B-2.3 Otowi #4**



### **Table B-2.3 — Otowi #4 (continued)**



<sup>a</sup> Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division

CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal Science Laboratories, and the University of Miami)<br>NATU = Natural uraniu

 $\degree$  U = Not detected.

 $R =$  Rejected.

### **Table B-2.4 La Mesita Spring**



### **Table B-2.4 — La Mesita Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

### **Table B-2.5 Guaje #5**



## **Table B-2.5 — Guaje #5 (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

#### **Table B-2.6 Water Canyon Gallery**



# **Table B-2.6 — Water Canyon Gallery (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

### **Table B-2.7 Upper Cañon de Valle Spring**







a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

#### **Table B-2.8 Spring 9b**



### **Table B-2.8 — Spring 9b (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

#### **Table B-2.9 Seven Springs**



### **Table B-2.9 — Seven Springs (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

#### **Table B-2.10 Pine Spring**



# **Table B-2.10 — Pine Spring (continued)**





# **Table B-2.10 — Pine Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S <sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

### **Table B-2.11 Pajarito Spring**



### **Table B-2.11 — Pajarito Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

#### **Table B-2.12 LAOI-1.1(A)**



### **Table B-2.12 — LAOI-1.1(A) (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

#### **Table B-2.13 Doe Spring**



# **Table B-2.13 — Doe Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

#### **Table B-2.14 Apache Spring**



### **Table B-2.14 — Apache Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

<sup>c</sup> U = Not detected.<br><sup>d</sup> R = Rejected.

#### **Table B-2.15 LAO-B Spring**



# **Table B-2.15 LAO-B Spring (continued)**



## **Table B-2.15 — LAO-B Spring (continued)**






## **Table B-2.15 — LAO-B Spring (continued)**



## **Table B-2.15 — LAO-B Spring (continued)**



a Pre-1997 = laboratory<br>EES = Earth and Environmental Science Division<br>CL= contract laboratory (Paragon Analytics Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, Coastal S

<sup>b</sup> na = Not analyzed.

 $\degree$  U = Not detected.

 $d$  R = Rejected.

## **Table B-3.1 Spring 1**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

## **Table B-3.2**

## **Sacred Spring**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

UM = University of Miami.  $b$  na = Not analyzed.

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

#### **Table B-3.3 Otowi #4**



<sup>a</sup> CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories),

#### **Table B-3.4 La Mesita Spring**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories),

UM = University of Miami.  $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $d$  TU = Tritium units. 1 TU = 3.193 pCi/L.

#### **Table B-3.5**

**Guaje #5** 



#### **Table B-3.6 Water Canyon Gallery**



<sup>a</sup> CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $d$  TU = Tritium units. 1 TU = 3.193 pCi/L.

<sup>a</sup> CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\mathcal{C}$  U = Not detected.

 $d$  TU = Tritium units. 1 TU = 3.193 pCi/L.

**Table B-3.7 Upper Cañon de Valle Spring** 



## **Table B-3.8 Spring 9b**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

<sup>a</sup> CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $b$  na = Not analyzed.

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

## **Table B-3.9**

**Seven Springs** 



## **Table B-3.10 Pine Spring**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\mathcal{C}$  U = Not detected.

 $d$  TU = Tritium units. 1 TU = 3.193 pCi/L.

# **Table B-3.11**

**Pajarito Spring** 



## **Table B-3.12 LAOI-1.1(A)**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

<sup>a</sup> CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\mathcal{C}$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>

#### **Table B-3.13 Doe Spring**



## **Table B-3.14 Apache Spring**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories), UM = University of Miami.

 $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $d$  TU = Tritium units. 1 TU = 3.193 pCi/L.

#### **Table B-3.15 LAO-B**



#### **Table B-3.15 — LAO-B (continued)**



#### **Table B-3.15 — LAO-B (continued)**



a CL = Contract laboratory (Paragon Analytics, Inc., General Engineering Laboratory, Huffman, Western Michigan University, Geochron Laboratories, and Coastal Science Laboratories),

UM = University of Miami.  $<sup>b</sup>$  na = Not analyzed.</sup>

 $\degree$  U = Not detected.

 $<sup>d</sup> TU$  = Tritium units. 1 TU = 3.193 pCi/L.</sup>